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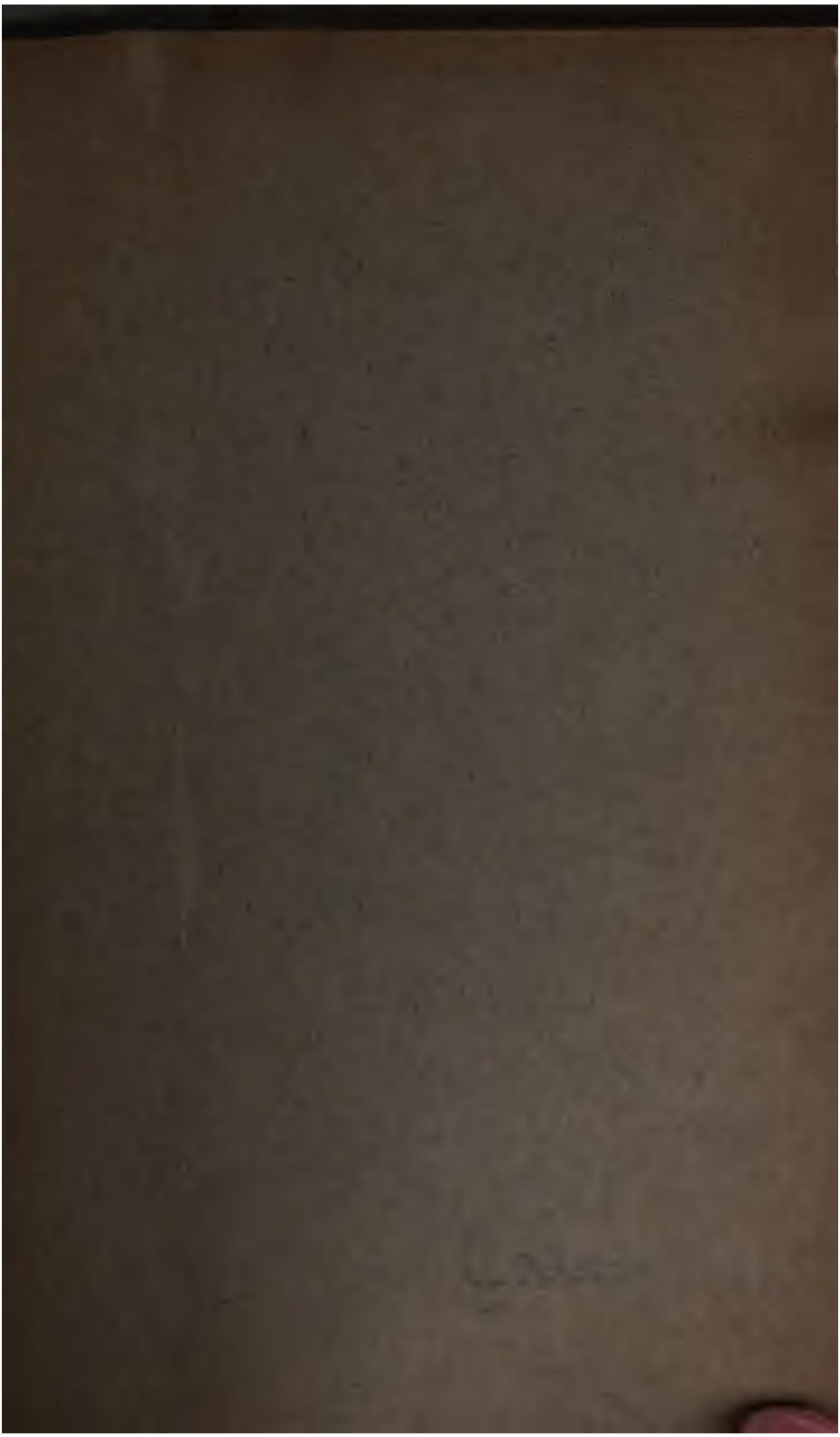

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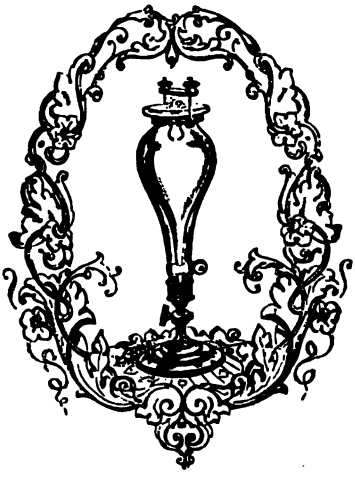

FOUNDED 1846.

HAND-BOOK

OF

CHEMISTRY.

BY

LEOPOLD GMELIN.

VOL. IX.

ORGANIC CHEMISTRY.

VOL. III.

ORGANIC COMPOUNDS CONTAINING FOUR AND SIX ATOMS OF CARBON.

TRANSLATED BY

HENRY WATTS, B.A., F.C.S.

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79 — 23 from top; *for* animine, *read* aniline.

576 — 4 ,, ; *for* 1850, *read* 1851.

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194 — 1 from top: *for* N^4, *read* H^4.

454 — 10 ,, ; *for* C^4H^5KO,C^2S^2, *read* $C^4H^5KO^2,C^2S^4$.

466 — 26 from bottom; *for* sulphur, *read* oxygen.

— 15 ,, ; *for* oxygen, *read* sulphur.

488 The composition of cyanic ether is incorrectly calculated; it should be:

6 C	36	50·70
5 H	5	7·04
N	14	19·72
2 O	16	22·54
$C^6H^5NO^2$	71	100·00

490 — 16 from bottom
491 — 9 from top
— 2, 10 from bottom
xviii — 10 from top
} ; *for* oxysulphocyanide, *read* oxysulphocyanate.

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501 The formula of nitroglycerine should be:

$$C^6N^3H^5O^{19} = C^6H^5X^3O^4,O^2;$$

and the calculation of its composition:

6 C	36	15·86
3 N	42	2·20
5 H	5	18·51
18 O	144	63·43
$C^6H^5X^3O^6$	227	100·00

ETHYLENE-SERIES.

(*Continued.*)

Acetone. $C^6H^6O^2 = C^4H^4O^2, C^2H^2$.

The Brothers Derosne. *Ann. Chim.* 63, 267.
Proust. *J. Phys.* 56, 200; also *A. Gehl.* 5, 578.
Chenevix. *Gilb.* 32, 191.
Macaire & Marcet, Jun. *Bibl. univers.* 24, 126; also *Schw.* 40, 348.
Matteucci. *Ann. Chim. Phys.* 46, 429; also *J. Chim. méd.* 7, 419.
Liebig. *Ann. Pharm.* 1, 223; also *Pogg.* 24, 285.
Dumas. *Ann. Chim. Phys.* 49, 208; also *N. Tr.* 26, 1, 309.
Robert Kane. *Pogg.* 44, 473; also *J. pr. Chem.* 15, 129.
Löwig & Weidmann. *Pogg.* 50, 299; also *J. pr. Chem.* 21, 54.
Zeise. With Chloride of Platinum: *Pogg.* 51, 6, 155 and 312; also *Ann. Pharm.* 41, 27; 43, 69; also *J. pr. Chem.* 20, 193. — With Phosphorus: *Ann. Pharm.* 41, 27; 43, 69; also *J. pr. Chem.* 26, 79 and 179. — With Sulphur and Ammonia: *Ann. Pharm.* 47, 24; also *J. pr. Chem.* 29, 371.
Stadeler. *Nachr. von der Gesellsch. der Wiss. zu Göttingen*, 1853, No 9, p. 121; *Chem. Gaz.* 1853, 341.

Pyroacetic Ether, Pyroacetic Spirit, Mesitic Alcohol, Brenzlicher Essigäther, Brenzlicher Essiggeist, Brenzessiggeist, Essiggeist, Mesitalkohol, Aceton, Ether pyroacétique (Derosne), *Esprit pyroacétique* (Chenevix). — Observed by Becher, Lemery, Rouelle, Stahl, Kunkel, and others, in the dry distillation of acetates. More exactly investigated by the above-mentioned chemists, especially by Kane, after the true composition had been pointed out by Liebig and Dumas.

Formation. 1. In the decomposition of acetic acid and its salts by heat (pp. 291, 295).—2. In the dry distillation of citric acid. (Robiquet.) Also in the dry distillation of sugar, gum, or starch with eight times its weight of lime (Fremy, *Ann. Chim. Phys.* 59, 7); also of tartaric acid. (Liebig, *Chim. org.*)

Preparation. By the dry distillation of an acetate. — The acetates of baryta and lime are the best adapted for this purpose; because they do not require so high a temperature to decompose them as the acetates of potash and soda, in the decomposition of which a large proportion of the acetone is resolved into empyreumatic oil, &c. (Pelouze), and because baryta and lime nevertheless retain the acetic acid too strongly to allow it to pass off undecomposed, as it does more or less from its combinations

with many heavy metallic oxides, which moreover often decompose part of the acetone by giving up oxygen to it. The more gradually the heat is raised during the distillation, the greater is the yield of acetone, whereas if the heat be suffered to rise too high, the acetone is resolved into empyreumatic oil, &c.

1. Perfectly dry acetate of baryta is distilled at a gradually increasing heat. (Liebig, Dumas.) Acetate of baryta when very pure and dry yields a colourless distillate, which is not acid, but consists wholly of acetone. (Liebig.) — 100 parts of acetate of baryta dried in vacuo are resolved by dry distillation into 72·2 per cent. of carbonate of baryta, 1·2 charcoal, 18·3 acetone, 6·6 water, and 1·7 gas (with loss). The distillate is freed from water by rectification over chloride of calcium.

2. Four pounds of neutral acetate of lead are intimately mixed with 2 pounds of lime, which is slaked during the trituration by the water of crystallization of the lead-salt; the mass introduced, while still hot from this hydration of the lime, into an iron quicksilver bottle (if left longer it swells up and is less covenient to introduce); the bottle laid in a nearly horizontal position in a furnace, but with its mouth slightly raised; a short downward-bent iron tube screwed into the mouth; the joints luted with a mixture of 2 pts. lime, 1 pt. sand, and a small quantity of common salt; and the iron tube connected with a long wide glass tube, which is kept cool by an ascending current of cold water, and passes into a receiver surrounded with ice. The heat is gradually raised to redness. The crude distillate, containing acetone together with a small quantity of water and two volatile empyreumatic oils, is shaken up with chloride of calcium and distilled in the water-bath. The distillate is mixed with coarsely pounded lime, set aside for a few days and frequently agitated, and three-fourths of the liquid distilled off: this distillate generally consists of pure acetone. The remaining portion of the distillate requires further purification. By this process, 4 pounds of acetate of lead yield from 5 to 5½ ounces of acetone (Zeise); — Gottlieb (*Ann. Pharm.* 52, 127) proceeds in a similar manner, but rightly uses only 1 pound of lime, whereby the process is accelerated and a much more abundant product obtained. 190 pts. (1 At.) of acetate of lead require to decompose them into acetate of lime and oxide of lead only 20 pts. (1 At.) of lime; the excess of lime decomposes part of the acetone. If the process succeeded perfectly, 190 pts. of acetate of lead should yield 29 pts. of acetone, or 4 pounds should yield 9¾ ounces.

Formerly acetone was obtained by distilling acetate of lead alone. Proust saturated the last portions of the distillate thereby obtained with potash, and rectified it, after separating the empyreumatic oil by mechanical means. — Chenevix, and likewise Macaire & Marcet, mixed the entire distillate obtained from the acetate of lead with potash; distilled off the more volatile portion; dissolved carbonate of potash in the distillate thus obtained, thereby causing the acetone to separate and rise to the surface; and then rectified it over chloride of calcium. — Gm. distilled the distillate obtained from acetate of lead, over milk of lime; then twice and only partially, in order to resinize the empyreumatic oil, over chloride of lime (which, however, according to Liebig, may convert the acetone into other products); then twice over chloride of calcium, but only partially, because towards the end an impure spirit passes over. — Liebig, in distilling acetate of lead, changed the receiver as soon as the water and acetic acid which first passed over were replaced by a combustible distillate which was nearly colourless, and had scarcely any acid reaction;

rectified this distillate in the water-bath; re-distilled the rectified product several times, always adding an equal volume of water, till the residual watery liquid, on the surface of which drops of oil were visible on the first distillation, no longer tasted of empyreumatic oil, and the distillate no longer exhibited any acid reaction; and finally, set the distillate aside in a stoppered bottle, together with a very large quantity of chloride of calcium; then decanted, and rectified it over fresh chloride of calcium.

The brothers Derosne prepared acetone from the last portions of liquid obtained by the distillation of crystallized verdigris; Trommsdorff obtained it by the dry distillation of acetate of soda.

It is difficult to obtain acetone quite free from empyreumatic oil, an impurity whose presence may be recognized by its odour.

Properties. — Transparent, colourless, very thin liquid. Sp. gr. 0·75 (Trommsdorff); 0·7864 (Chenevix); 0·7921 at 18° (Liebig); 0·822 (Gm.); 0·88 (Proust); 48° Bm. or about 0·792 (Derosne); 0·8140 at 0° (H. Kopp, *Pogg.* 72, 1). Does not solidify even at −15° (Chenevix). Boiling point: 55·6° (Liebig); 56° at 0·76 met. pressure (Dumas); 56·25° (Gm.); 57° (Reichenbach); 59° (Chenevix); 56·3° at 0·76 met. pressure (H. Kopp). Evaporates in the air, producing a considerable degree of cold. (Trommsdorff.) Vapour-density: 2·0025 (Dumas); 2·022 (Kane). — Has a pungent odour which, according to Trommsdorff, resembles that of ether, and somewhat that of garlic; according to Chenevix, it resembles those of the oils of peppermint and bitter almonds; according to Gm., it is sweetish, like that of acetic ether. Its taste is biting like that of camphor, and burning (Trommsdorff); burning at first, afterwards cooling and somewhat urinous (Chenevix); strongly refreshing, but with a biting and burning character; the after-taste sweetish and pungent. (Gm.) — Neutral:

			Liebig.	Dumas.	Kane.	Macaire & Marcet.	Matteucci.
6 C	36	62·07	62·15	62·44	62·5	55·30	59·86
6 H	6	10·34	10·45	10·20	10·2	8·20	6·40
2 O	16	27·59	27·40	27·36	27·3	36·50	33·74
$C^6H^6O^2$	58	100·00	100·00	100·00	100·0	100·00	100·00

	Vol.	Density.	Or:	Vol.	Density.
C-vapour	6	2·4960	Aldehyde-vapour	1	1·5252
H-gas	6	0·4158	Methylene-gas	1	0·4853
O-gas	1	1·1093			
Acetone-vapour	2	4·0211		1	2·0105
	1	2·0105			

Acetone is regarded by Chancel as a conjugated compound of the methylene-series, $= C^4H^4O^2, C^2H^2$ (VII, 214), and by Kane as an alcohol, probably containing the nucleus C^6H^4 and $= C^6H^4, H^2O^2$. In favour of Chancel's and against Kane's view, it may be alleged that, in the decomposition of acetone by oxidation, no compounds are formed containing C^3 (*e. g.*, not acrolein, $C^6H^4O^2$, or acrylic acid, $C^6H^4O^4$), but compounds belonging to the ethylene and methylene series, such as acetic and formic acid (VII, 215); that all other alcohols are formed from nuclei containing equal numbers of carbon and hydrogen atoms, *e. g.* C^2H^2, C^4H^4, and C^6H^{12}; and lastly, that the products which Kane obtained from acetone and regarded as corresponding to ether, chloride of ethyl, &c., show, by

their slight volatility, and by various other characters, that they should be regarded as compounds containing 12 or more atoms of carbon. On the other hand, if Chancel's view be adopted, it is difficult to assign any rational formula to Kane's products, such for example as *chloride of pteleyl*, C^6H^3Cl, and *nitrite of pteleyl*, $C^6H^3NO^4 = C^6H^3X$ (*vid.* p. 23). Such being the uncertainty which exists respecting the real constitution of these products, it will be best to consider them in the form of an appendix, immediately after acetone.

¶ According to the more recent views of Chancel and Gerhardt, acetone may be regarded as aldehyde in which 1 At. H is replaced by methyl; in fact, aldehyde and acetone are formed upon the type hydrogen, HH, just as acetic acid and acetate of methyl are formed from the type water (HH)O ; thus (VII, 17):

$\left.\begin{matrix}H\\H\end{matrix}\right\}$ Hydrogen.		$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	Water.
$\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}$ Aldehyde.		$\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$	Acetic acid.
$\left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}$ Acetone.		$\left.\begin{matrix}C^2H^3O\\CH^3\end{matrix}\right\}O$	Acetate of methyl.

Städeler likewise regards acetone as aldehyde, in which 1H is replaced by methyl; thus: aldehyde $= C^2\left\{\begin{matrix}H\\C^2H^3\end{matrix}\right\}O^2$; acetone $= C^2\left\{\begin{matrix}C^2H^3\\C^2H^3\end{matrix}\right\}O^2$. ¶.

Decompositions. — 1. Acetone passed through a *red-hot tube* is converted, with deposition of charcoal and formation of a small quantity of water into the oil (dumasin), which generally goes over with acetone produced by the dry distillation of acetates.

2. Acetone is more easily *set on fire* than alcohol, and burns completely away, with a bright white flame, which is blue at the edges, and does not deposit soot. (Trommsdorff. Chenevix.) The flame is reddish yellow, faintly blue at the lower part; it has the same degree of brightness as that of ether, and only smokes a little when a piece of cold metal is held above it. The combustion produces nothing but carbonic and water (Trommsdorff); no acetic acid. (Liebig.) — Air mixed with vapour of acetone is likewise inflammable. — Acetone sprinkled in the dark on a red-hot iron exhibits a blue flame (alcohol does not). (Brewster, *Ed. J. of Sc.*, 4, 140). — Acetone may be preserved without alteration in a bottle containing air. (Liebig.)

3. Dry *Chlorine gas* passed into dry acetone is abundantly absorbed, with rise of temperature and evolution of hydrochloric acid gas, without altering the appearance of the acetone (if, however, water be present, chloroform is precipitated in the form of an oil). If the passage of the chlorine be continued, and the liquid at the same time heated from without till the action ceases, the acetone is found to be converted into a heavy oil containing chlorine. (Liebig.) This oil is Kane's mesitic chloral:

$$C^6H^6O^2 + 4Cl = C^6H^4Cl^2O^2 + 2HCl.$$

But it is impossible to replace the whole of the hydrogen by chlorine, even at 100° and in sunshine. (Dumas & Kane, *Ann. Chim. Phys.* 73, 94.) — Unsatisfactory experiments with chlorine had been previously made by Macaire & Marcet, and by Matteucci. — When acetone is distilled with aqueous chloride of lime, chloroform is evolved and carbonate of lime precipitated. (Liebig.)

¶. Several substitution-products are obtained by the action of a mixture of chlorate of potash and hydrochloric acid on acetone. These compounds are oily, have an intolerable odour, and produce inflammation when they come in contact with the skin, these effects being produced in greatest intensity by the compounds containing the smallest proportion of chlorine. The products which are poorer in chlorine are decomposed by potash, with production of a brown colour and separation of resinous masses, whereas the addition of potash to those which are richer in chlorine effects no change in the colour. The compounds act in the same manner with strong sulphuric acid. They are all much more soluble in cold than in hot water; a saturated cold solution becomes turbid even with the heat of the hand, whilst a heat of 50° — 60° separates the greater portion of the dissolved compound in heavy colourless drops. The same compounds are formed by the action of nascent chlorine on other organic bodies; especially by the action of a mixture of chlorate of potash and hydrochloric acid on kinic, citric, or gallic acid. The aid of sunshine is required to effect the replacement of more than 5 At. H by Cl. (Städeler.)

Pentachlorinated Acetone, $C^6HCl^5O^2$, is a tolerably mobile, colourless liquid, having a burning aromatic taste, and a peculiar odour resembling that of chloral. It does not solidify at — 20°, volatilizes gradually in the air, and boils at about 190°. Sp. gr. between 1·6 and 1·7. With 8 At. water, it forms a compound which crystallizes in rhombic tables, and melts at about 16°. Its aqueous solution has a distinct acid reaction. (Städeler.)

Hexachlorinated Acetone, $C^6Cl^6O^2$, is obtained by the action of chlorine gas, aided by sunshine, on citric acid. Resembles the preceding compound in every respect. With 2 At. water it forms a crystalline hydrate which melts between 15° and 16°. Plantamour, who discovered this compound, assigned to it the formula $C^6Cl^5O^6$; but Städeler shows that its composition agrees equally well with the above formula. (Städeler.) ¶.

4. Acetone in contact with *Bromine* and caustic potash yields bromoform. (Dumas, *Ann. Chim. Phys.* 56, 120; also *Pogg.* 31, 654.) — Acetone prepared from citric acid likewise yields bromoform. When a small quantity of caustic potash is added to the acetone, and then an excess of bromine, bromoform separates in the form of a reddish oil, which may be decolorized by a small quantity of potash. (Cahours, *N. Ann. Chim. Phys.* 19, 493.) — Is acetic acid also formed, according to the equation:

$$C^6H^6O^2 + 6Br + 2HO = C^2HBr^3 + C^4H^4O^4 + 3HBr,$$

or rather acetate of potash, according to the following:

$$C^6H^6O^2 + 6Br + 3KO = C^2HBr^3 + C^4H^3KO^4 + 2KBr + HBr + HO?$$

With *Iodine* and caustic potash, acetone does not form iodoform or iodate of potash, but deposits a blackish pitch-like substance, which decomposes when heated, is insoluble in water, but dissolves in alcohol. (Bouchardat, *J. Pharm.* 23, 5.)

5. The solution of *Phosphorus* in acetone turns acid when kept for some weeks, and more quickly when heated, even in perfectly air-tight vessels, the change consisting in the formation of three acids, all containing carbon, hydrogen, oxygen and phosphorus, viz., *Phosphacetic*, *Acephoric*, and *Acephosgenic acid*, together with an insoluble compound of carbon and phosphorus. This transformation is not attended with the evolution of any gas or vapour; excepting that of acetone, part of which

compound remains undecomposed, and may be distilled off as a neutral liquid.

Acephoric Acid.

Pure acetone is heated nearly to the boiling point for 24 hours with a very large excess of phosphorus, in a flask which is fitted with a long ascending tube, having a bulb in the middle and the part beyond the bulb bent downwards, the bulb being surrounded with cold water, so that the acetone which rises into it in vapour may be condensed and flow back. The cooling of the bulb is then discontinued and the undecomposed acetone distilled over; the thin syrupy residue poured off from the remaining phosphorus, and a sufficient quantity of acetone distilled from it to convert it into a thick syrup; this syrup diluted with six times its bulk of water, whereupon it becomes milky from separation of a light yellow body containing phosphorus; the filtrate mixed with oxide of lead, set aside in a close vessel, and frequently agitated till it becomes neutral or retains but a slight degree of acidity; and the solution of acephorate of lead separated by filtration from the white powder consisting of phosphacetate, acephosgenate, and a small quantity of phosphate of lead. The lead is precipitated from the filtrate by sulphuretted hydrogen; the liquid filtered; saturated with lime; and the acephorate of lime, purified by solution in alcohol (which leaves behind a small quantity of admixed acephosgenate of lime), and by precipitating the filtrate with ether (any phosphacetate of lime that may be present then remaining in solution). To obtain the acid in the free state, it is best to separate it from the aqueous solution of its lead-salt by sulphuretted hydrogen.

The aqueous acid leaves when evaporated a light yellow varnish having a very sour taste. In this state it gives off, when heated nearly to redness, a gas (which does not take fire spontaneously) and thick white fumes, leaving after the ignition, a carbonaceous mass from which water extracts phosphoric acid, while flocculent charcoal remains.

The acid dissolves readily in water. Its salts are either gummy or pulverulent; do not give off phosphuretted hydrogen when heated; dissolve readily in water and also in alcohol. Their aqueous solution is not precipitated even by subacetate of lead, but only by nitrate of silver, which after a while (immediately, with the aid of heat) produces a brown-black precipitate.

The *Ammonia-salt* becomes acid when its solution is evaporated in vacuo. — The *Soda-salt* dissolved in alcohol has a slight alkaline reaction. — The *Lime-salt* is perfectly neutral. When subjected to dry distillation it yields products having an acid reaction. The phosphorus which it contains is not completely oxidized by strong nitric acid, but readily by heating with carbonate of soda and nitrate or chlorate of potash.—The *Lead-salt*, when its aqueous solution is evaporated, is partly converted into an insoluble residue. (Zeise.)

Phosphacetic Acid.

The white pulverulent mixture of phosphacetate, acephosgenate, and phosphate of lead, is diffused in water and decomposed by sulphuretted hydrogen; the filtrate saturated with lime; the solution of phosphacetate of lime separated by filtration from the undissolved acephosgenate and

phosphate; the filtrate, which would be liable to decomposition by evaporation, mixed with nitrate of lead to precipitate the phosphacetic acid as a lead-salt; the phosphacetate of lead diffused in water, and decomposed by sulphuretted hydrogen; and the filtrate evaporated.

The phosphacetic acid then remains as a light yellow varnish having a very sour taste. When heated, it gives off a large quantity of gas, which sometimes takes fire and burns feebly, and thick white fumes, leaving phosphoric acid mixed with flocculent carbonaceous matter.

The acid dissolves very readily in water. Its salts do not give off phosphuretted hydrogen when heated. — The *Baryta-salt* (mixed with acephorate) is a colourless or yellowish neutral mass, sometimes crystalline, sometimes like varnish. It yields by dry distillation, a gas, a small quantity of colourless distillate and carbonaceous residue, and does not take fire when heated in contact with the air. It is instantly turned brown by immersion in oil of vitriol, and black if heat be applied. Dissolves readily in water, but very slightly in alcohol, which indeed precipitates it from the aqueous solution. The aqueous solution of the baryta-salt yields a white pulverulent precipitate with nitrate of lead; a greenish brown, gelatinous precipitate with protochloride of copper; a white bulky precipitate with corrosive sublimate; and with nitrate of silver a copious white precipitate, which turns black in half an hour at ordinary temperatures and immediately when heated. (Zeise.)

Acephosgenic Acid.

After the aqueous solution of phosphacetate of lime has been filtered from the acephosgenate and phosphate (*vid. sup.*) the lime in these two salts is replaced by soda; the phosphate of soda separated by crystallization from the acephosgenate; the solution of the latter precipitated by nitrate of lead; and the acephosgenate of lead treated with sulphuretted hydrogen to separate the free acid.

On evaporating the aqueous solution, the acid remains in the form of a pale yellow, strongly acid varnish, which is resolved by heat into a large quantity of gas (free from phosphuretted hydrogen), white fumes, and phosphoric acid mixed with charcoal.

Acephosgenic acid dissolves readily in water. Its salts do not give off phosphuretted hydrogen when heated. Many of them are insoluble or sparingly soluble in water, so that acephosgenate of soda precipitates a great number of salts; with nitrate of silver it forms a yellow precipitate (resembling phosphate of silver) which turns brown-black, slowly at ordinary temperatures but quickly when heated. (Zeise.)

Insoluble Compound containing Carbon and Phosphorus.

When the same portion of phosphorus is repeatedly treated with fresh quantities of acetone, there remains a greyish yellow viscid mass, having the consistence of turpentine. If the acid liquid be poured off from this mass, and the residue treated, first with water to remove the remaining acid, then with sulphide of carbon to take up the free phosphorus which has not been acted on, a dark yellow powder remains behind. This substance is not altered when gently heated in contact with air, but if subjected to a stronger heat, yields phosphorus and a carbonaceous residue.

(Zeise.) [It remains to be determined whether this compound is free from hydrogen and oxygen.]

Sulphur forms with acetone products similar to those obtained with phosphorus; but acts more slowly. — *Sulphide of phosphorus* forms with it a peculiar acid, and an oil which has a powerful odour but no acid reaction. (Zeise.)

6. Strong *Nitric acid* decomposes acetone with violent evolution of heat and nitric oxide gas, and formation of mesitic aldehyde ($C^6H^4O^2$), nitrite of pteleyl ($C^6H^3NO^4$), acetic acid, oxalic acid, and cyanuric acid. — Acetone heated with nitric acid of 1·25, gives off nitric oxide with violence and leaves a syrup from which oxalic acid crystallizes. (Trommsdorff.) — Distilled with ½ vol. strong nitric acid, it deposits a drop of oil in the retort, and finally leaves therein oxalic acid and a carbonaceous residue; the distillate thereby obtained, if redistilled after neutralization with potash, leaves acetate and nitrate of potash, and yields a distillate of peculiar character. (Chenevix.) — Acetone placed in a test-tube above an equal volume of strong nitric acid, soon becomes heated to violent percussive ebullition, which lasts a long time, giving off nitric oxide having a bitter ethereal odour, and leaving a small quantity of a liquid which contains oxalic acid, is rendered turbid by the presence of drops of oil, and yields more oil when treated with water. This oil is yellow, thickish, has a taste which is aromatically sweet at first, but afterwards sharp and burning, and leaves for an hour a burning sensation on the tongue. (Gm.) — When a mixture of 3 vol. acetone and 3 vol. nitric acid is twice gently heated in a retort, till it is brought into a kind of fermentation, but evolves no gas or nitrous fumes, and half the mixture distilled over at a gentle heat, the residue in the retort consists of a liquid which throws down a large quanity of cyanate of silver [probably cyanurate] from the nitrate; and two distillates are obtained, viz., a watery liquid, which likewise gives a copious precipitate with nitrate of silver, and a transparent colourless oily liquid, which has an aromatic odour, boils from 80° to 100°, forms acetic acid when kept for some time, contains 66·43 p. c. carbon, 10·84 hydrogen, and 22·73 oxygen, and is, therefore = C^4H^3O,H = *Hydrure d'Aldehyde*. This oil, when treated with chlorine gas, is converted, with formation of hydrochloric acid, into another oil which contains 35·2 per cent. of carbon, 4·5 of hydrogen, and 60·3 O + Cl, and is therefore C^4H^3O,Cl = *Chlorure d'Aldehyde* (Laurent, *Ann. Chim. Phys.* 66, 318.) A mixture of 2 vol. acetone and 1 vol. strong nitric acid gives off when heated a large quantity of nitrous fumes, and froths up strongly enough to break the retort if the heat be continued. If the liquid be heated only till it begins to froth, the frothing checked by immersing the vessel in cold water, the liquid again heated till it cools, the vessel again cooled, and this treatment frequently repeated, the mixture, when subsequently treated with water, yields a pale yellow oily precipitate, consisting of mesitic aldehyde and nitrate of pteleyl, in which the mesitic aldehyde predominates in proportion to the extent to which the decomposition has been carried. Dilute nitric acid exerts scarcely any action, even when heated, but lets the acetone pass over unaltered (Kane.)

7. Acetone heated with aqueous *Iodic* acid forms a peculiar oil, without separation of iodine. (Millon.)

8. Acetone mixed with *Oil of Vitriol*, evolves great heat and forms a dark brown, or if rise of temperature be prevented, a light brown liquid. According to the proportions in which the liquids are mixed and the rise

of temperature which takes place, the product may be mesitic ether ($C^6H^5O=C^{12}H^{10}O^2$), mesitylene ($C^6H^4=C^{12}H^8$), a waxy substance, mesitylosulphuric, permesitylosulphuric, or sulphurous acid.—2 vol. acetone heated with 1 vol. oil of vitriol, leave a carbonaceous residue, and yield two distillates smelling of sulphurous acid, the upper yellow, and the lower, which is the largest in quantity, white. (Chenevix.) — A mixture of acetone and oil of vitriol does not give off any ether when heated; but when diluted with water and neutralized with baryta, it yields sulphate of baryta and a soluble baryta-salt, probably sulphovinate. (Liebig.) — If the liquids be gradually mixed in equal volumes and kept cool, a dark brown mixture is formed, containing mesitylene, a waxy matter, and a small quantity of mesitic ether, which substances rise to the top in a thickish stratum on the addition of water. When 1 pt. of acetone and 2 pts. of oil of vitriol are mixed rapidly and without cooling, sulphurous acid is evolved, and a dark brown mixture formed, containing permesitylosulphuric acid, together with a small quantity of mesitylosulphuric acid. 2 vol. acetone and 1 vol. sulphuric acid produce mesitylosulphuric acid. The latter mixture evaporated at a gentle heat, yields a distillate of aqueous sulphurous acid, and a yellowish oil floating upon it; this oil, which amounts to $\frac{1}{4}$ of the acetone, is a mixture of acetone, mesitylene, and another oil having a higher boiling point than mesitylene. (Kane.) — The watery liquid which passes over together with the mixture of mesitylene and acetone, on distilling a mixture of 2 vol. acetone and 1 vol. oil of vitriol, contains sulphurous acid and acetic acid, which may be separated by baryta; in the retort there remains a greenish waxy matter mixed with sulphur. (Plantamour.)

9. Acetone mixes with glacial *Phosphoric acid*, evolving heat, and forming a dark brown mass containing but a small quantity of mesitylophosphoric acid. (Kane.)

10. Acetone absorbs a large quantity of *Hydrochloric acid gas*, forming a brown liquid. (Chenevix.) This brown, thickish, heavy, and very acid liquid contains a large quantity of chloride of mesityl ($C^6H^5Cl=C^{12}H^{10}Cl^2$), which may be precipitated by water, but likewise contains mesitic ether and undecomposed acetone. (Kane.) The brown liquid distilled over carbonate of potash yields two distillates, the one transparent and colourless, the other, which is the lighter of the two, having a yellowish colour. The latter has an aromatic odour, and a hot, oily taste; is but slightly miscible with acetone; dissolves in 40 parts of water; gives no indication of hydrochloric acid with any reagent; but yields an abundant precipitate with nitrate of silver, when burnt on the top of it. (Chenevix.) Aqueous hydrochloric acid forms with acetone a dark brown mixture, from which the acetone may be recovered nearly in its original state by distillation. (Kane.)

11. Acetone mixed with twice its weight of *Pentachloride of Phosphorus* is likewise converted into chloride of mesityl. (Kane.)

12. When acetone is brought in contact with *Iodine* and *Phosphorus* at the same time, large quantities of hydriodic acid gas are evolved, iodide of mesityl (probably C^6H^5I) is formed, and may be distilled over; also iodide of pteleyl (perhaps C^6H^3I) which remains suspended in the residual liquid in the form of golden-yellow scales; and mesitylo-hypophosphorous acid, which separates in silky needles as the liquid cools. (Kane.) In this process, a large quantity of acetone passes over, and only a small quantity of iodide of mesityl; the residual syrup contains no mesitylo-hypophosphorous acid, but when mixed with water, separates into two

layers, the upper of which appears to be iodide of mesityl, while the lower contains phosphorous acid and hydriodic acid. A yellowish red deposit of phosphorous oxide is likewise formed (Plantamour, *Ann. Pharm.* 31, 327.)

13. Acetone heated with aqueous *Bichromate of Potash* [and sulphuric acid?], yields large quantities of acetic and carbonic acids, but no formic acid (Dumas & Stas, *Ann. Chim. Phys.* 73, 149; also *Ann. Pharm.* 35, 160):

$$C^6H^6O^2 + 8O = C^4H^4O^4 + 2CO^2 + 2HO.$$

Gottlieb also (*Ann. Pharm.* 52, 130) obtained by this means neither acetic acid nor propronic acid $C^6H^6O^4$. — Acetone distilled with peroxide of maganese and dilute sulphuric acid passes over unchanged; but if strong sulphuric acid be used, the products formed are the same as when no manganese is present. (Kane.)

14. Acetone mixed with dry *Bichloride of Platinum* becomes heated, assumes a black-brown colour, and yields hydrochloric acid, a volatile substance which attacks the eyes powerfully, acechloride of platinum, aceplatinous oxide, and crude platinum-resin. (Zeise.) If pulverized bichloride of platinum be mixed with a small quantity of acetone into a paste, which has a black-brown colour, the mixture when kept in a bottle for a day, gives off hydrochloric acid and a substance which attacks the eyes, and becomes gritty in consequence of the formation of crystallized acechloride of platinum [amounting to 20 per cent. of the bichloride of platinum used]. — A solution of 1 pt. bichloride of platinum in 10 pts. acetone, which is red-brown at first, soon assumes a black-brown colour, so dark as to render it opaque; yields by distillation acetone and a large quantity of hydrochloric acid (a peculiar odour being also emitted), and leaves a syrup. In treating this syrup with water, the greater part remains undissolved in the form of a black-brown tarry matter, which is *crude platinum-resin;* the watery filtrate begins, after ten minutes, to deposit acechloride of platinum as a yellow crystalline powder, which after some days, amounts to 5 per cent of the bichloride of platinum used. When the dark brown liquid poured off from this deposit is distilled to one-half, it yields, with much frothing, but without evolution of gas, a liquid containing hydrochloric acid, acetone, and a peculiar substance; while the liquid which remains in the retort becomes decolorized, and deposits a very large quantity of a black powder, consisting of aceplatinous oxide, ultimately mixed with a little metallic platinum. If, on the contrary, the dark-brown liquid decanted from the acechloride of platinum be left to evaporate at ordinary temperatures over oil of vitriol and hydrate of potash, there remains a syrup rich in hydrochloric acid, and resolved by water into crude platinum resin and a brown liquid, which, on standing, deposits acechloride of platinum (Zeise; see these products among the *Addenda to Acetone*, p. 31.)

¶ 15. A solution of *Ammonia* in acetone, exposed to spontaneous evaporation, leaves a colourless, syrupy residue which does not crystallize by exposure to great cold. It is soluble in water, alcohol, and ether; does not turn brown when boiled with potash, and reduces silver-salts like aldehyde-ammonia. This compound, when kept, gradually undergoes spontaneous decomposition, and is converted into an organic base, to which Städeler gives the name of *Acetonine*. This base is more rapidly formed when acetone saturated with ammonia is heated to 100° in a sealed tube. The composition of acetonine agrees with the formula

$C^{18}H^{18}N^2$, so that it bears to acetone the same relation that amarine bears to oil of bitter almonds. (Städeler, *Chem. Gaz.* 1853, 341.) — Pure acetonine is a colourless alkaline liquid, having a peculiar, somewhat urinous odour, and a burning taste. It dissolves in ether, and alcohol, and also in water; potash added to the aqueous solution separates the acetonine in oily drops. Aqueous acetonine acquires a milky turbidity throughout when gently heated, like aqueous coniine. — Its platinum-compound, $C^{18}H^{19}N^2Cl, PtCl^2$ crystallizes in orange-yellow, shining, four-sided prisms, with oblique terminal faces. It is insoluble in ether, but soluble in water and in alcohol containing a small quantity of hydrochloric acid. (Städeler.) — *Binoxalate of Acetonine*, $C^{18}H^{18}N^2, 2C^2O^3, 4HO$, crystallizes from its boiling saturated alcoholic solution in delicate white prisms, which dissolve readily in water but not in ether. Gives off 1 At. water at 100°, and is decomposed at a somewhat higher temperature. (Städeler.) ¶

16. The chief products formed by the simultaneous action of *Ammonia* and *Sulphur* on acetone, are Thakcetone, Akcethine, Therythrine, Melathine, a brown resin, and Elathine. (Zeise.)

a. When acetone is saturated with dry ammoniacal gas, then with sulphur, then again with ammoniacal gas, and then again with sulphur — whereby it becomes heated and assumes, first a green, then a brownish yellow, and then a brown colour — there is ultimately obtained a red-brown, viscid, strongly alkaline mass, having a very offensive odour, like that of sulphuretted hydrogen. This mass, which dissolves completely in alcohol or acetone, is resolved, when treated with ether, into an insoluble brown resin, and a brown solution from which water throws down *Thakcetone.*

b. When the red-brown, transparent mass is gradually heated in a distillatory apparatus from 50° to 95°, and carefully excluded from moisture, ammonia and hydrosulphate of ammonia are first given off, and immediately afterwards a light yellow liquid passes over, containing ammonia, hydrosulphate of ammonia, water, a small quantity of acetone, and a small quantity of a dissolved oil.

c. Between 95° and 120°, two distillates are obtained, the lower watery and yellow, the upper oily and brown.

d. Between 120° and 200°, a viscid oil is obtained (consisting chiefly of *Elathine*), and a crystalline sublimate composed of hydrosulphate of ammonia, *Akcethine*, and other products.

e. If the distillation be interrupted at 200°, and the brown-black residue, which up to that temperature is in a state of tranquil fusion, be treated with ether, (which chiefly extracts *Akcethine* and a brown resinous body), and afterwards exhausted with alcohol, a residue is left, consisting of *Melathine;* the alcoholic extract contains *Therythrine*, which is precipitated in the form of a brown-red powder by water. The ethereal extract exposed to a gradually increasing heat, yields, first, pure ether, then ether containing oil, then a brown oil mixed with water, and from 170° to 200°, a crystalline sublimate consisting chiefly of *Akcethine.*

f. If the distillation of the ethereal extract (*e*) be stopped at 200°, the residue in the retort again treated with ether, and afterwards with alcohol, ethereal and alcoholic extracts are obtained resembling the former, that is to say, the second ethereal extract again yields *Akcethine* by distillation; and if the alternation be repeated eight times successively, the result is still the same.

g. If, on the other hand, the distillation of (*d*) be further continued

from 200° to 275°, the brown-black residue froths up strongly; yields a few volatile products; and then solidifies to a greyish black, spongy, brittle, coaky mass, three-fourths of which consists of *Melathine* (which remains behind after the mass has been exhausted with alcohol), acetone, sulphide of carbon, and ether.

Thakcetone. — Obtained as in (*a*) in the form of a yellow precipitate, or better in the following manner: The red-brown, viscid mass *a* is neutralized with oxalic acid dissolved in ether; the liquid filtered from oxalate of ammonia, therythric matter, and resinous matter; the filtrate mixed with water; the excess of oxalic acid precipitated by means of gypsum; the filtrate evaporated; the residue exhausted with alcohol; and the solution filtered from sulphate of ammonia, and left to evaporate over oil of vitriol. The thakcetone then remains in the form of a brownish yellow, amorphous, neutral varnish. When subjected to dry distillation, it froths up strongly, yields hydrosulphate of ammonia and a dark brown oil smelling like oil of hartshorn, and leaves a large quantity of charcoal rich in nitrogen and sulphur. Heated with potash, it gives off a large quantity of ammonia. It dissolves abundantly in water forming a strongly coloured solution, readily also in alcohol, sparingly in ether. The concentrated aqueous solution forms with nitrate of silver, a yellowish white precipitate which turns brown when heated, but does not precipitate neutral or basic acetate of lead.

Akcethine. — The sublimate obtained as in (*e*) and (*f*) is dissolved in the smallest possible quantity of hot alcohol; the solution left to evaporate to a certain extent in the air; and the resulting crystals pressed between paper, and purified by recrystallization. — Lemon-yellow, transparent, highly lustrous, inodorous rhombohedrons. They melt at about 150° to a clear, sulphur-yellow liquid, which becomes red-brown and viscid at a stronger heat, but solidifies in a yellow radiating mass on cooling. At a still higher temperature, the akcethine is converted into a yellowish vapour, and sublimes without decomposition in the form of a yellowish crystalline body; if the neck of the retort be allowed to get too hot, a small quantity of hydrosulphate of ammonia is evolved with deposition of charcoal. When heated in the air, it fuses to a black-brown mass, without previously taking fire. It is decomposed by hot nitric acid with separation of sulphurous flocks, and yields sulphuric acid when boiled. With concentrated potash at a boiling heat, it yields ammonia It dissolves sparingly in water, and in cold dilute hydrochloric, sulphuric, or nitric acid; more readily in ether; still more in alcohol and acetone. The yellow, slightly alkaline solutions may be boiled without decomposition; they do not precipitate the salts of iron or lead, but yield with nitrate of silver, (after a time only, if it be dilute,) a copious, bulky, light yellow precipitate, which collects in five minutes into a snow-white powder.

Therythrine. — The brown-red powder precipitated by water from the alcoholic extract, as mentioned in (*e*), fuses like resin somewhat above 100°; gives off hydrosulphate of ammonia and a brown offensive-smelling oil at a stronger heat; and leaves a lustrous, very combustible charcoal. It is nearly insoluble in water, but dissolves abundantly, without decomposition and with a deep brown-red colour, in oil of vitriol, also in strong potash-solution. It dissolves abundantly, with brown-red colour, in sulphide of carbon, alcohol, and acetone, sparingly in ether. The alcoholic solution, when evaporated, leaves the therythrine in the form of a dark-red, brittle, amorphous resin; it does not precipitate acetate of

lead, but forms a dark-red precipitate with nitrate of silver. — When the thick, red-brown mass produced in the preparation of thakcetone, is treated with oxalic acid dissolved in ether, there remains a mass from which alcohol extracts a substance resembling therythrine, which may be precipitated therefrom by water.

Melathine. — Obtained in the process described in (*g*). Black. When subjected to dry distillation, it yields, without fusion, a gas rich in sulphuretted hydrogen, together with a trace of oil, and leaves a difficultly combustible charcoal. When ignited with hydrate of potash, it gives off a large quantity of ammonia, leaving a residue rich in sulphide of potassium; this compound is also formed, but in small quantity, when melathine is boiled with strong potash. Melathine heated with nitric acid, forms a brown solution, from which water throws down a large quantity of brownish flocks, while the liquid remains brown. With oil of vitriol also it forms a brown solution, from which water throws down brown flocks. It is quite insoluble in hydrochloric and in water, and dissolves but sparingly in sulphide of carbon, alcohol, ether, and acetone.

Brown resinous body. — Produced in large quantity simultaneously with the preceding products. May be obtained in the preparation of thakcetone by means of oxalic acid dissolved in ether (p. 12). When the dark brown ethereal liquid formed in this process is filtered and mixed with a sufficient quantity of water, it deposits a pitchy substance, which must be redissolved in ether, reprecipitated by water, and dissolved in alcohol; the alcoholic solution, after being filtered from a black substance, is then evaporated in vacuo over oil of vitriol, the residue dissolved in ether, and the solution again evaporated in vacuo. By this repeated evaporation, a volatile oil mixed with the resin is ultimately driven off; evaporation at a higher temperature might produce decomposition. — Another method of obtaining the resinous body is to exhaust with ether the residue which remains after distilling the thick red-brown mass (*e*) at 200°; precipitate the filtrate with water, which leaves akcethine in solution; dissolve the precipitate in ether; and evaporate the solution, first at a gentle heat, then in vacuo over oil of vitriol. The resinous body obtained by either of these processes is amorphous, decomposible by heat, insoluble in water, but soluble in ether, alcohol, and acetone.

Elathine. — Occurs principally in the oil which passes over (as in *d*), in the distillation of the thickred-brown mass between 120° and 180°. The oil is dissolved in ether; the filtrate mixed with alcohol; and water added, whereby an aqueous mixture is produced, chiefly containing akcethine, and an oily, alkaline liquid, which must be neutralized with an ethereal solution of oxalic acid. The liquid is then filtered; the filtrate shaken up with water as long as the water acquires a yellow colour; then dried by agitation with chloride of calcium; and finally distilled with a fresh receiver. Ether passes over first, then, between 140° and 150°, the elathine, and finally a brown turbid oil. — Elathine is a brownish-yellow oil, lighter than water, and having a peculiar and very offensive odour; suffers partial decomposition when distilled; takes fire with difficulty, and burns with a very smoky flame, producing sulphurous acid. When set aside with strong potash-solution and agitated, it produces a tolerably large quantity of sulphide of potassium. Its solution in alcoholic potash, which is clear at first, gradually deposits a white powder. It is insoluble in water.

An indigo-blue, indifferent body containing sulphur, may likewise be obtained from the thickish, red-brown mass. (Zeise.)

¶. 17. *Action of Ammonia and Bisulphide of Carbon on Acetone.*— When pure acetone is mixed with an equal volume of sulphide of carbon and about twice its volume of ammonia, laminated crystals, resembling ice, are formed after a few days in the lower stratum of liquid; but these disappear after a while, and are succeeded by larger crystals of a yellow colour. These yellow crystals are insoluble in water, sparingly soluble in ether, and dissolve with decomposition in warm alcohol and boiling hydrochloric acid. After drying in vacuo, they exhibit a composition corresponding to the formula $C^{30}H^{26}N^3S^9$, and may be regarded as a compound of *Sulphocarbamate of Sulphide of Acetonyl with Sulphocyanide of Acetonyl*, $2C^6H^6S,C^2H^3NS^3+2(C^6H^6,CyS^2)$. A cold alcoholic solution of this compound mixed with a similar solution of bichloride of platinum, forms a brownish yellow, non-crystalline precipitate composed of $C^{30}H^{26}N^3S^9,3Pt.S^2$; and with a cold alcoholic solution of corrosive sublimate a white precipitate containing $C^{30}H^{26}N^3S^9,27HgS,18HgCl$. (Hlasiwetz, *J. pr. Chem.* 51, 355; *Ann. Pharm.* 76, 294; *Jahresber.* 1850, 391). The compound $C^{30}H^{26}N^3S^9$ boiled with caustic potash, gives off ammonia and forms oxide of mesityl (p. 24). When heated to its melting point, it yields a lower stratum of acetone and bisulphide of carbon, and an upper stratum, containing a large quantity of sulphide of ammonia; a small quantity of sublimate consisting of white needles is formed at the same time. The compound boiled with alcohol gives off ammonia and carbonic acid, and forms sulphide of ammonium, together with a small quantity of a crystalline compound, which when dried in vacuo, has the composition $C^{36}H^{34}N^6S^6$, and is regarded by Hlasiwetz as a compound of *Acetonylamide with Sulphocyanide of Acetonyl*$=2(C^6H^6,NH^2)+3(C^6H^6,CyS^2)$.—*Hydrosulphate of Sulphacetonyl*$=3C^6H^6S,HS+8HO$ is obtained in the form of a colourless oil, by the dry distillation of a mixture of mesitylosulphate of lime and monosulphide of potassium.

According to Städeler (*Chem. Gaz.* 1853, 341), the yellow crystalline body formed by the action of ammonia and sulphide of carbon upon acetone, has not the composition assigned to it by Hlasiwetz, but is the *Hydrosulphate of Carbothiacetonine*, a base composed of $C^{20}H^{18}N^2S^4$, which agrees pretty well with the analysis given by Hlasiwetz. The platinum-compound of this base is $C^{20}H^{18}N^2S^4,PtS^2$, and the mercurial precipitate obtained by Hlasiwetz is nothing but $HgCl,2HgS$, having a small quantity of hydrochlorate of carbothiacetonine adhering to it.

18. *Thiacetonine;* probably $C^{18}H^{19}NS^4$. This base, which appears to be identical with Zeise's akcethine, (p. 12), is formed by the simultaneous action of *ammonia* and *sulphuretted hydrogen* upon acetone; apparently also by boiling an alcoholic solution of hydrosulphate of carbothiacetonine:

$$C^{20}H^{18}N^2S^4,2HS + 4HO = C^{18}H^{19}NS^4 + NH^3 + 2CO^2 + 2HS?$$

crystallizes in strongly lustrous, yellowish rhombohedrons; has an alkaline reaction; and dissolves readily in dilute acids, ether, alcohol, and acetone, but is rather difficult of solution in water. (Städeler.). ¶

19. Pulverized *Hydrate of Potash* mixed with anhydrous acetone become strongly heated; colours it light yellow; and swells up within it to a dark brown mass, which, on addition of water, is resolved into an oily mixture of xylite-oil and xylite-resin, and an aqueous solution, containing wood-spirit and acetate of potash, together with undecomposed acetone. If 2 parts of hydrate of potash be gradually added to 1 pt. of acetone cooled from without, and the mass, after standing for 8 days, be

mixed with water, a brown oil rises to the surface. — *a.* The oil when distilled with water, fresh portions of which are added as long as any oil passes over with it, is resolved into *Xylite-oil*, which passes over, and *Xylite-resin* which remains behind. — The *Xylite-oil* is purified by agitation with chloride of calcium and distillation, during which process it boils pretty regularly at 200°. It contains 81·32 per cent. C, 10·19 H, and 8·47 O; it is therefore $=C^{12}H^{9}O$, and perfectly agrees, both in composition and in odour, taste, boiling point, and in its solubility in ether and alcohol, with the xylite-oil obtained from lignone. — *Xylite-resin* purified by solution in alcohol and evaporation of the filtrate, is red-brown and brittle; becomes tough between 16° and 20°; is insoluble in caustic potash; and contains 79·48 p.c. C, 9·65 H, and 10·87 O, agreeing therefore with the xylite-resin obtained from lignone. — *b.* The aqueous, yellow, alkaline liquid is decolorized by neutralization with sulphuric acid, a trace of resin being separated at the same time; and yields by distillation, first, acetone and wood-spirit, (which may be separated from the acetone by distilling the mixture of the two from chloride of calcium, the wood-spirit being thereby retained), then at a higher temperature, a large quantity of acetic acid, and leaves a residue quite free from organic matter. (Löwig & Weidmann.) The equations which these chemists give for the formation of the above compounds are improbable. Hydrate of potash moistened with acetone and exposed to the air, absorbs oxygen, and forms a small quantity of acetate of potash, chiefly, however, if not exclusively, when the acetone contains empyreumatic oil. (Liebig.)

20. Acetone passed in the state of vapour over *heated hydrate of potash*, is resolved into marsh-gas and carbonate of potash, partly also, probably when the heat is not very great, into acetate and formiate of potash :

$$C^{6}H^{6}O^{2} + 2(HO,KO) = C^{4}H^{8} + 2(KO,CO^{2});$$

and

$$C^{6}H^{6}O^{2} + 4HO + KO = C^{4}H^{3}KO^{4} + C^{2}HKO^{4} + 6H.$$

Vapour of acetone passed through a glass or iron U-tube, in which hydrate of potash is heated to fusion, yields marsh-gas mixed with a small quantity of carbonic acid. (Persoz. *Rev. scientif.* 1, 51.) — Similarly, acetone-vapour passed over a heated mixture of lime and hydrate of potash — which first becomes yellow, then again white, and takes up carbonic acid — yields marsh-gas mixed with only 2 or 3 per cent. of hydrogen. (Dumas & Stas, *Ann. Chim. Phys.* 73, 149.) — When acetone vapour is passed over a hot mixture of lime and hydrate of potash, a large quantity of acetate and formiate of potash is produced. (Gottlieb, *Ann. Pharm.* 52, 130.)

21. *Potassium and Sodium* in contact with acetone, become intensely heated, and yield products similar to those which are formed by hydrate of potash. — Potassium in contact with acetone gives off great heat, and forms a thickish, yellowish brown liquid, containing acetate of potash, on the top of which floats a green oil, smelling like oil of peppermint. (Matteucci.) — This oil is the solution of a viscid resinous matter in acetone. (Dumas, *Ann. Chim. Phys.* 49, 208.) — Sodium forms with acetone a thick yellow-brown mass, the action being attended with frothing and rise of temperature. (Gm.) — When potassium acts in considerable quantity, it causes evolution of gas, and a rise of temperature

sufficient to set the liquid on fire, whereupon charcoal is separated. If the potassium be added gradually to the acetone, each piece being introduced as the former disappears, and the liquid cooled from without, the decomposition takes place quietly, with gentle ebullition, but without evolution of any permanent gas. A brownish, strongly alkaline powder is deposited at first, but subsequently dissolves. The ultimate product dissolves in water, with separation of an oil. This oil is a mixture of xylite-oil (80·81 p. c. C, 10·32 H, and 8·87 O), and xylite-resin (containing 79·75 p. c. C, 9·14 H, and 12·11 O). — The red, aqueous, alkaline solution, saturated with sulphuric acid, deposits a few resinous flocks, and yields by distillation, first, acetone, and perhaps also wood-spirit, and then a small quantity of acetic acid. (Löwig and Weidmann; *comp.* also Löwig, *Pogg.* 42, 410.)

¶ 22. *Quick lime* acts on acetone in the same manner as hydrate of potash, converting it into xylite-oil;

$$2C^6H^6O^2 - 3HO = C^{12}H^8O.$$

When acetone is mixed with finely pounded lime, no action takes place at first; but in the course of a few weeks, the acetone disappears, forming with the lime a solid mass, which yields but little acetone when distilled in the water-bath. On the addition of water, the lime slakes, after which a small quantity of acetone may be distilled off; and if the heat be continued, the water which passes over is accompanied by a slightly yellow oil, which begins to boil a little above 100°, but distils over for the most part between 200° and 220°. The residual mass of lime treated with hydrochloric acid, yields a small quantity of coloured resin. (Völckel, *Ann. Pharm.* 82, 63.) ¶.

Combinations. — Acetone mixes in all proportions with *Water.* (Chenevix, Gm., Liebig.)

At ordinary temperatures, it dissolves a small quantity of *Phosphorus* and a still smaller quantity of *Sulphur.* (Chenevix.)

It slowly dissolves hydrate of potash, forming a deep yellow solution (Chenevix) [decomposition takes place at the same time]; it is not miscible with strong potash-ley. (Liebig.)

Most salts which are soluble in alcohol, are insoluble in acetone; such, for example, is the case with *Chloride of Calcium.* (Liebig.) — But chloride of calcium mixed with acetone swells up and forms a white mass. (Gm.) — When an aqueous solution of chloride of calcium is shaken up with acetone and then left at rest, two layers of liquid are formed, the upper of which is acetone, the lower, aqueous chloride of calcium containing acetone; but a portion of the acetone separates from the lower stratum, and rises to the top whenever it is heated. (Liebig & Pelouze, *Ann. Pharm.* 19, 287.) — The solution of chloride of calcium in alcohol or wood-spirit is capable of taking up a large quantity of acetone. (Reichenbach.) When 1 vol. acetone is added to 3 vol. of a saturated solution of chloride of calcium, the acetone is dissolved, but chloride of calcium is at the same time precipitated; on adding more acetone to this mixture, all the chloride of calcium separates out; if instead of the acetone, a few drops of water be added, the acetone rises to the surface and forms a separate stratum above the aqueous and alcoholic solution of the chloride of calcium. (Liebig, *Ann. Pharm.* 10, 320.) — ¶ According to Hlasiwetz (*Ann. Pharm.* 76, 294) acetone forms a

definite compound with chloride of calcium and water. A mixture of pulverized chloride of calcium and rectified acetone assumes a pasty consistence at first, then becomes hot, and forms a dry mass, which at 100° gives off mere traces of a liquid having an ethereal odour; if more water be added, pure acetone distils over from 80° to 83°. ¶

Acetone mixes uniformly with aqueous *Terchloride of Gold*; but on adding to the solution a further quantity of dry terchloride of gold, acetone having a yellow colour and containing terchloride of gold rises to the surface of the watery liquid. (Derosne.)

Acetone mixes with *Ether* and *Alcohol*, and with many *compound Ethers*, in all proportions.

It mixes with *Volatile oils*, and dissolves many *Camphors*, *Fats*, and *Resins*.

Addenda to Acetone.

Decomposition-products of Acetone, which do not at present admit of exact systematic classification.

Mesitylene or Mesitylol. $C^6H^4 = C^{12}H^8 = C^{18}H^{12}$.

Kane. *Pogg.* 44, 474; also *J. pr. Chem.* 15, 131.

Hofmann. *Chem. Soc. Qu. J.* 2, 104; *Ann. Pharm.* 71, 121; abstr. *Pharm. Centr.* 1849, 233; 1850, 65; *Compt. rend.* 28, 130; *Instit.* 1849, 25; *N. J. Pharm.* 16, 310; *Jahresber.* 1849, 445.

When 2 vol. acetone are distilled at a gentle heat with 1 vol. oil of vitriol, the liquid froths slightly, aqueous sulphurous acid distils over, and with it a yellowish oil which floats on the top and amounts to about ¼ of the acetone. This product is washed with water, distilled in the water-bath till the admixed acetone is volatilized, and then at a stronger heat to obtain the mesitylene, which must be collected in a separate receiver; the distillation must not, however, be carried on to dryness, otherwise the distillate will be contaminated with an oil of higher boiling point. The mesitylene thus obtained is purified by leaving it for 24 hours in contact with chloride of calcium, then decanting and distilling again. (Kane.)

Transparent, colourless, very light oil, having a slightly alliaceous odour, and boiling at about 135·5°. (Kane.) According to Hofmann, however, mesitylene purified as completely as possible by repeated rectification, boils between 155° and 160°;—according to Cahours, between 162° and 164°. Vapour-density = 2·914. (Cahours, *Ann. Chim. Phys.* 70, 101; *vid. infra*.)

				Kane.		Vol.	Density.
12 C	72	90	89·61	C-vapour	12	4·9920
8 H	8	10	10·34	H-gas	8	0·5544
$C^{12}H^8$	80	100	99·95	Mesitylene-vapour	2	5·5464
					1	2·7732

Kane assumes the formula C^6H^4, regarding the compound as the

nucleus which with H^2O^2 forms acetone, just as ethylene, C^4H^4, with H^2O^2 forms alcohol. Cahours, in accordance with his determination of the vapour-density, prefers the formula $C^{12}H^8$; but the boiling point 135° determined by Kane, is too high even for this. (Schröder, *Pogg.* 67, 49.) According to Gerhardt's calculation (VII, 57), this boiling point corresponds exactly with the formula $C^{18}H^{12}$. Perhaps Kane's mesitylene was contaminated with a small quantity of the less volatile oil which he mentions as passing over towards the end of the distillation; and therefore exhibited too high a boiling point. — ¶. The boiling point found by Hofmann is however higher still, viz., between 155° and 160°; moreover, the action of nitric acid on mesitylene, which gives rise to the three compounds, $C^{18}H^{11}X$, $C^{18}H^{10}X^2$, and $C^{18}H^9X^3$ (pp. 20, 22) clearly shows that the formula $C^{18}H^{12}$ is the correct one.

But according to the vapour-density above given (2·914) as determined by Cahours, the formula $C^{18}H^{12}$ would represent the vapour as trisatomic instead of diatomic, which is contrary to the usual character of organic compounds. Hofmann therefore suggested (*Chem. Soc. Qu. J.* 2, 112) that the vapour-density might be subject to variations similar to those observed in sulphur, and in certain of the volatile fatty acids. (VII, 54.) — The difficulty has, however, been completely removed by a subsequent determination of the vapour-density made by Cahours (*Chem. Soc. Qu. J.* 3, 17), from which it appears that the vapour is really diatomic. The specimen of mesitylene used in this last-mentioned determination was purified by several rectifications and final distillation from anhydrous phosphoric acid; it boiled between 162° and 164°. and exhibited exactly the theoretical composition of mesitylene. The vapour-density was found in one experiment, to be 4·345; in another, 4·282. The composition of mesitylene is therefore as follows:

					Vol.		Density.
18 C	108	....	90	C-vapour.....	18	....	7·4880
12 H.....	12	....	10	H-gas	12	....	0·8316
$C^{18}H^{12}$	120	....	100	Vapour of $C^{12}H^8$	2	....	8·3196
					1	....	4·1598 ¶

Mesitylene burns with a bright but very smoky flame. It absorbs chlorine gas in large quantity and with great evolution of heat, afterwards gives off hydrochloric acid, and solidifies to an acicular mass of chloride of pteleyl, C^6H^3Cl [or terchloromesitylene, $C^{18}H^9Cl^3$]. — Boiling nitric acid converts it into mesitic aldehyde. (Kane.) — A mixture of equal parts of fuming nitric and fuming sulphuric acid converts it immediately, and without rise of temperature, into the crystalline compound $C^6H^3NO^4$. (Cahours, *Compt. rend.* 24, 555.) [This compound differs from Kane's nitrite of pteleyl, which has the same composition, but is liquid; Cahours's compound should, perhaps, be regarded as $C^{12}H^6X^2$, or $C^{18}H^9X^3$]. — Mesitylene is likewise decomposed by oil of vitriol, but not by aqueous alkalis. (Kane.)

Mesitylene dissolves *Iodine*, forming a deep brown liquid, which is not altered by exposure to sunshine. (Kane.) — *Bromine* converts it into a white crystalline compound. (Hofmann.)

Iodide of Pteleyl (or Teriodomesitylene).

KANE. *Pogg.* 44, 487; also *J. pr. Chem.* 15, 146.

Kane gave the name of *Pteleyl* (from πτελέα, the elm) to the radical C^6H^3, because he formerly supposed it to exist in ulmic acid.

When acetone is distilled with iodine and phosphorus, the residual liquid contains shining, golden-yellow scales of iodide of pteleyl; these, after a sufficient addition of water, may be thrown upon a filter, and then washed and dried, whereupon they lose their lustre, and form a golden-yellow powder. This substance, when heated nearly to redness, rises in vapour, and condenses in the form of a gold-coloured sublimate. But when its vapour is passed through a red-hot tube, iodine is set free and charcoal deposited. It is insoluble in water, but dissolves in ether, and separates from the solution in shining spangles. Its formula is probably C^6H^3I (Kane), [or $C^{18}H^9I^3$].

¶ Terbromomesitylene. $C^{18}H^9Br^3$.

HOFMANN. *Chem. Soc. Qu. J.* 2, 108.

When bromine is added drop by drop to mesitylene, waiting each time till the heat evolved has subsided, and taking care to keep the mesitylene in excess, a white crystalline compound is formed, which may be freed from hydrobromic acid by washing with water, in which it is perfectly insoluble. Two or three crystallizations from boiling alcohol render it absolutely pure. — White needles, which volatilize without decomposition, and are not changed by boiling with potash or ammonia. (Hofmann.)

			Hofmann.
18 C	108	30·25	30·70
9 H	9	2·52	2·79
3 Br	240	67·23	66·68
$C^{18}H^9Br^3$	357	100·00	100·17

A compound of similar composition and properties was previously obtained by Cahours, who assigned to it the formula $C^{12}H^6Br^3$. ¶

Chloride of Pteleyl. C^6H^3Cl, (or Terchloromesitylene. $C^{18}H^9Cl^3$).

KANE. *Pogg.* 44, 486; also *J. pr. Chem.* 15, 145.

Chlorine gas is passed through mesitylene till the liquid solidifies in an acicular mass, which is then dissolved in hot ether and crystallized by cooling, the undecomposed mesitylene remaining in the mother-liquid. The product is purified by recrystallization, and the crystals dried between paper, but not in contact with the air.

White, shining, four-sided prisms, resembling sulphate of quinine, volatilizing only at a strong heat, but without decomposition. They may also be sublimed without alteration in dry ammoniacal gas, and are not decomposed by alcoholic potash. (Kane.)

			Kane.
6 C	36·0	48·39	49·91
3 H	3·0	4·03	4·17
Cl	35·4	47·58	
C^6H^3Cl	74·4	100·00	

¶ Nitromesitylene. $C^{18}H^{11}NO^4=C^{18}H^{11}X$.

Cahours. *Compt. rend.* 30, 319; *Chem. Soc. Qu. J.* 3, 185.

Formed by treating mesitylene with fuming nitric acid, not in excess, and carefully cooling the mixture during the action.

18 C	108	65·45
11 H	11	6·67
N	14	8·48
4 O	32	19·40
$C^{18}H^{11}X$	165	100·00

This compound, when treated with an alcoholic solution of potash, becomes heated and evolves two products on distillation. One of these is a liquid, which is produced in very small quantity only, and exhibits the properties of an alkaloid; the other, which is solid, dissolves very readily in alcohol, and separates from it by spontaneous evaporation in tabular crystals of great beauty; it is isomeric with nitromesitylene.

¶ Binitromesitylene. $C^{18}H^{10}N^2O^8=C^{18}H^{10}X^2$.

Hofmann. *Chem. Soc. Qu. J.* 2, 110.

Obtained by boiling mesitylene with moderately strong nitric acid. After a few distillations, the whole of the mesitylene is converted into a crystalline compound, which may be purified by washing with water and recrystallization from alcohol. With dilute nitric acid, a less definite result is obtained, the mesitylene being converted, after repeated distillation, into a yellow oil, which shows a tendency to crystallize, but appears to be a mixture.

This compound crystallizes in fine needles, often several inches long, and in appearance resembling those of ternitromesitylene (*vid. inf.*). Volatilizes without decomposition. Dissolves with great facility in alcohol. (Hofmann.)

			Hofmann.
18 C	108	51·42	51·07
10 H	10	4·76	4·98
2 N	28	13·35	
8 O	64	30·47	
$C^{18}H^{10}X^2$	210	100·00	

¶ Nitromesidine. $C^{18}H^{12}N^2O^4 = C^{18}H^{10}AdX$.

MAULE. *Chem. Soc. Qu. J.* 2, 116; *Ann. Pharm.* 71, 137; abstr. *Pharm. Centr.* 1850, 69; *Jahresber.* 1849, 402.

Obtained by the action of sulphuretted hydrogen on binitromesitylene:

$$C^{18}H^{10}N^2O^8 + 6HS = C^{18}H^{10}(NO^4)(NH^2) + 4HO + 6S.$$

When an alcoholic solution of binitromesitylene is submitted to the action of sulphuretted hydrogen, the liquid assumes a dark colour and deposits gradually a large quantity of sulphur, the odour of the sulphuretted hydrogen being at the same time destroyed. This treatment is continued for several days, till the sulphuretted hydrogen is no longer decomposed. On the addition of hydrochloric acid, sulphur is again precipitated; and on separating this by filtration, a clear liquid is obtained which when mixed with potash or ammonia, yields a copious precipitate of impure nitromesidine. By repeatedly dissolving this impure product in hydrochloric acid and reprecipitating by an alkali, small quantities of still adhering sulphur are separated, and the substance gradually assumes a bright yellow colour. One or two crystallizations from alcohol now suffice to render it absolutely pure.

Properties. Long needle-shaped crystals of a golden yellow colour. Melts below 100°, and solidifies on cooling in a mass of radiated needles. Volatilizes without decomposition at 100°, giving off a vapour which burns with a bluish flame. Dissolves very readily in alcohol and ether, and sparingly in water, to which it imparts a faint yellow colour. The solutions have an unpleasant bitter taste, and are neutral to test paper.

	Dried at 100°.			Maule.
18 C	108	....	60·00	..... 60·01
12 H	12	....	6·67	..... 6·74
2 N	28	....	15·55	..... 16·31
4 O	32	....	17·78	..... 16·94
$C^{18}H^{12}N^2O^4$	180	....	100·00	..... 100·00

Decompositions. Bromine acts violently on nitromesidine, forming a dark oily liquid. — An alcoholic solution of nitromesidine yields with chlorine a pinkish solid substance soluble in boiling ether.

Combinations. Nitromesidine dissolves readily in acids, forming crystalline salts, which however are very unstable; all those yet obtained, excepting the phosphate and the platinum-salt, being decomposed by mere contact with water. They are soluble in alcohol, and their solutions have an acid reaction.

Phosphate. — *a. Terbasic.* — A solution of nitromesidine in aqueous phosphoric acid yields this salt in leafy crystals of a beautiful lemon-yellow colour, which may be washed with water without decomposition.

	Dried at 100°.			Maule.
54 C	324·0	....	50·75	50·54
39 H	39·0	....	6·10	6·35
6 N	84·0	....	13·16	
P	31·4	....	4·92	4·86
20 O	160·0	....	25·07	
$3C^{18}H^{12}N^2O^4,PO^5+3Aq$	638·4	....	100·00	

b. Monobasic? If a large excess of phosphoric acid be used, an acid salt is obtained, which appears to contain only 1 At. of nitromesidine.

Sulphate. White silky crystals decomposed by water.

Hydrochlorate. A solution of nitromesidine in dilute hydrochloric acid, evaporated and left to cool, deposits this salt in colourless needles which are decomposed by water.

	Dried at 100°.			Maule.
18 C	108·0	....	49·90	49·52
13 H	13·0	....	6·00	6·01
2 N	28·0	....	12·93	
Cl	35·4	....	14·78	
4 O	32·0	....	16·39	16·32
$C^{18}H^{12}N^2O^4,HCl$	216·4	....	100·00	

Nitrate. Formed by dissolving nitromesidine in dilute nitric acid. The solution evaporated with an excess of free nitric acid, is decomposed when the evaporation reaches a certain point, red nitrous fumes being disengaged and a red oily product remaining.

Platinum-salt. When an excess of bichloride of platinum is added to a hot saturated solution of hydrochlorate of nitromesidine, the liquid on cooling deposits the double salt in groups of yellow crystals, which may be purified by washing with water and crystallization from alcohol. (Maule.)

				Maule.
18 C	108·0	....	27·96	28·07
13 H	13·0	....	3·36	3·50
2 N	28·0	....	7·25	
Pt	99·0	....	25·64	25·49
3 Cl	106·2	....	27·49	
4 O	32·0	....	8·30	
$C^{18}H^{12}N^2O^4,HCl,PtCl^2$	386·2	....	100·00	

¶ Ternitromesitylene. $C^{18}H^9N^3O^{12}=C^{18}H^9X^3$.

CAHOURS. *N. Ann. Chim. Phys.* 25, 39.
HOFMANN. *Chem. Soc. Qu. J.* 2, 110.

Formed by the action of a mixture of equal parts of fuming nitric and fuming sulphuric acid (Cahours), or of fuming nitric acid alone (Hofmann), on mesitylene.

When pure mesitylene is added drop by drop and with agitation, to the mixture of fuming nitric and sulphuric acid, a white flocculent

substance separates out, which when dry is seen to be an aggregation of slender interlaced needles. If the process be carefully performed, scarcely any rise of temperature is perceptible. When a sufficient quantity of the product is obtained, the liquid must be diluted with water and washed on a filter, till the wash-water no longer exhibits any acid reaction. The product is then dried by pressure between bibulous paper, and lastly treated with alcohol, which does not dissolve it but removes a substance which gives it a rose-colour. As thus prepared, it is colourless, and crystallizes in delicate needles. It may be obtained in a state of still greater purity by sublimation at a gentle heat. It is then perfectly white and assumes the form of very delicate, shining needles, resembling flowers of antimony. It may also be obtained in very well defined prismatic needles by adding mesitylene drop by drop to the mixture of sulphuric and nitric acid, till the liquid begins to exhibit turbidity, and leaving it to evaporate in a very damp atmosphere. The product then separates slowly and in well defined crystals.

Volatilizes without decomposition. Insoluble in cold alcohol (Cahours); very sparingly soluble, even in boiling alcohol (Hofmann); dissolves readily in acetone. (Maule.)

			Cahours.		Hofmann.
18 C	108	42·35	42·26	42·43	42·14
9 H	9	3·53	3·44	3·67	3·87
3 N	42	16·48	16·55		
12 O	96	37·64			
$C^{18}H^9X^3$	255	100·00			

Ternitromesitylene is slowly decomposed by sulphuretted hydrogen, a basic compound being formed. (Maule.)

By acting on mesitylene with fuming nitric acid unmixed with sulphuric acid, Cahours obtained merely a red-brown heavy oil, having a strong pungent odour, but not exhibiting any definite constitution (*vid.* also Kane, *inf.*): Hofmann, on the other hand obtained crystallized ternitromesitylene, just as with the mixture of nitric and sulphuric acid. ¶

Nitrite of Pteleyl. $C^6H^5NO^4=C^6H^5X$.

KANE. *Pogg.* 44, 489; also *J. pr. Chem.* 15, 148.

Obtained by heating a mixture of 2 vol. acetone and 1 vol. strong nitric acid till it begins to froth; cooling the vessel, by immersion in cold water, till the effervescence subsides; heating it again till the effervescence recommences; then cooling it once more, — and so repeatedly, but not too often; then diluting the mixture with 6 times its bulk of water; washing the pale yellow liquid which sinks to the bottom with water, till it is quite free from acid; and finally removing the water by means of chloride of calcium. This process yields nitrite of pteleyl contaminated with mesitic aldehyde, the quantity of which is greater as the decomposition has taken place more rapidly; too rapid action must therefore be avoided, inasmuch as there is no means of separating the mesitic aldehyde completely.

Thin liquid, heavier than water. Does not volatilize at 100°. Has a pungent, somewhat sweetish taste.

			Kane.
6 C	36	42·35	44·57
3 H	3	3·53	4·02
N	14	16·47	
4 O	32	37·65	
$C^6H^3NO^4$	85	100·00	

According to Kane, this compound $= C^6H^3O,NO^3$; according to the substitution-theory, it is $C^6H^3(NO^4) = C^6H^3X$. It is polymeric with ternitromesitylene.—The excess of carbon and hydrogen found in the analysis, is attributed by Kane to the presence of mesitic aldehyde.

The compound, when strongly heated, explodes violently, even small quantities shattering the containing glass vessel; hence it cannot be purified by distillation. The explosion is accompanied by evolution of nitrous fumes and separation of a considerable quantity of charcoal which covers the bottom of the vessel. Paper saturated with the compound burns like tinder when dried [how is it dried?]—The compound gradually decomposes when immersed in water.—It dissolves in alkalis, forming a dark brown solution. (Kane.)

This compound, when dissolved in absolute alcohol, and heated with potash, appears to yield acetic ether. (Chancel, *N. Ann. Chim. Phys.* 7, 356.)

Mesitic Ether or Oxide of Mesityl = $C^{12}H^{10}O^2$.

KANE. *Pogg.* 44, 475; also *J. pr. Chem.* 15, 133.

Preparation. 1. Acetone and oil of vitriol are gradually mixed in equal volumes, in a vessel immersed in cold water, so as to prevent any great rise of temperature, which would cause the abstraction of all the water and formation of mesitylene, and also to avoid evolution of sulphurous acid. The dark brown mixture, containing a small quantity of mesitic ether together with mesitylene and a waxy substance, is left to cool completely, and then mixed with twice its bulk of water; after which the mixture is set aside, the thickish upper stratum removed by means of a pipette, and the smaller portion of it distilled off from lime; the mesitic ether then passes over first, but the process does not yield it quite pure.

2. The impure alcoholic solution of chloride of mesityl is mixed with a sufficient quantity of alcoholic potash to render it strongly alkaline; then warmed for some time; diluted with 8 times its bulk of water; the yellow oil which separates out in small quantity dried over chloride of calcium, and distilled into two receivers, the acetone which had remained mixed with the mesityl used in the preparation passing over first, and then the mesitic ether, while the mesitylene being less volatile remains behind. The chloride of mesityl is decomposed by the potash in such a manner as to yield mesitic ether and chloride of potassium.

Transparent, colourless, very thin liquid, which boils at 120°, has an aromatic odour like that of peppermint, and burns with a bright flame and very little smoke. (Kane.)

			Kane.
12 C	72	73·47	73·16
10 H	10	10·20	10·55
2 O	16	16·33	16·29
$C^{12}H^{10}O^2$	98	100·00	100·00

According to Kane, it is C^6H^5O, which would make it identical with oxide of allyl.

Pyroacetic Oil or Dumasin.

KANE, *Pogg.* 44, 494; also *J. pr. Chem.* 13, 69. — R. Marchand, *J. pr. Chem.* 13, 69. — Heintz, *Pogg.* 68, 277.

Formed by passing acetic acid or acetone through a red-hot tube, and by the dry distillation of those acetates which yield acetone, especially if they are suddenly exposed to a strong heat, whereby the acetone produced at first is subsequently decomposed.

The oil cannot be completely separated from the admixed acetone by fractional distillation. If to such a mixture there be added oil of vitriol, then water, then carbonate of lime, drops of the empyreumatic oil rise to the surface, and may be freed by distillation from the pitchy resin formed at the same time. (Marchand.) Heintz agitates the empyreumatic oil obtained by the dry distillation of 2 pts. acetate of lead and 1 pt. lime, repeatedly with water, to remove the acetone; dries it for a long time over chloride of calcium, then decants, and boils it for some minutes in contact with the air, to volatilize the remainder of the acetone; distils, till the boiling point, which is 130° at first, has risen to 200°, whereupon a blackish tar remains behind; and separates from the distillate the more volatile portion, which is the pure pyroacetic oil.

Thin, transparent and colourless oil; boils at 120° (Kane); between 120° and 130° (Heintz.) Vapour density 5·204 (Kane); has an aromatic odour (Heintz.)

Calculation, according to Kane.		Kane.			
10 C	60	78·94	78·82	C-vapour	10	4·1600
8 H	8	10·53	10·46	H-gas	8	0·5544
O	8	10·53	10·72	O-gas	½	0·5546
$C^{10}H^8O$	76	100·00	100·00	Oil-vapour	1	5·2690

Calculation, according to Heintz		Heintz.				
		a.	*b.*	*c.*	*d.*	*e.*
12 C	72	73·47	73·49	74·64	75·51	77·62	79·66
10 H	10	10·20	10·30	10·40	10·34	9·40	8·77
8 O	16	16·33	16·21	14·96	14·15	12·98	11·57
$C^{12}H^{10}O^2$	98	100·00	100·00	100·00	100·00	100·00	100·00

a is the analysis of the pure oil which boils between 120° and 130°; the distillates *b*, *c*, *d*, *e*, obtained by continuing the distillation with a rising boiling-point, become continually richer in carbon and poorer in hydrogen and oxygen. (Heintz.)

Since Kane or Heintz cannot have made a mistake of 5 per cent. in the carbon, we must suppose that they analyzed different products: hence it would appear that more than one empyreumatic oil is obtained from acetic acid or acetone, a supposition which is confirmed by the analyses *b*, *c*, *d*, *e*.

The pure oil *a* analyzed by Heintz, is by him considered to be

identical with Kane's mesitic ether. It burns with a bright, smoky flame. When treated with nitric acid, it solidifies and is converted into an acid which dissolves in potash, forming a dark-red solution, and is precipitated therefrom by the stronger acids.

Mesitic Aldehyde. $C^6H^4O^2 = C^{12}H^8O^4$.

KANE. *Pogg.* 44, 491; also *J. pr. Chem.* 15, 150.

This compound is formed by carefully heating 2 vol. acetone with 1 vol. strong nitric acid, and diluting with water; but as thus obtained, it is always contaminated with nitrite of pteleyl (*q. v.*). To obtain it pure, mesitylene is boiled with nitric acid, fresh quantities of which are continually added till no further action appears to take place; the product is then washed with water, and dried over chloride of calcium.

Heavy yellow liquid of sweetish astringent taste.

			Kane.
6 C	36	64·29	64·83
4 H	4	7·14	7·11
2 O	16	28·57	28·06
$C^6H^4O^2$	56	100·00	100·00

Dissolves sparingly in water, but readily in alkaline liquids, forming a yellowish brown solution. — It absorbs ammoniacal gas with great avidity, forming a brown resinous mass. This compound of mesitic aldehyde with ammonia may be obtained in the crystalline state by solution in water and careful evaporation. Its aqueous solution mixed with nitrate of silver, immediately forms a yellow precipitate which blackens when heated; the reduction is however incomplete. But oxide of silver precipitated from the nitrate by a small quantity of potash, is immediately reduced on addition of mesitic aldehyde, sometimes to a black powder, sometimes to a metallic and somewhat specular coating. (Kane.)

Iodide of Mesityl or Hydriodate of Mesitylene.

KANE, *Pogg.* 44, 478; also *J. pr. Chem.* 15, 137.

1. Acetone mixed in a retort with iodine and phosphorus, and heated, gives off a large quantity of hydriodic acid gas, and yields a distillate coloured dark by iodine and smelling of hydriodic ether. If this distillate be treated with water to remove hydriodic acid and with potash to remove free iodine, and thereby decolorized, it becomes coloured again, both when left to itself and when immersed in water, in consequence of the separation of free iodine, which is deposited, together with charcoal, at a later stage of the decomposition. At all events, iodide of mesityl thus prepared is very impure, being contaminated with varying quantities of acetone, mesitic ether, and frequently also of mesitylene, and consequently gives very variable results on analysis. It is partially decomposed by distillation.

2. A purer iodide of mesityl is obtained by introducing into a tube

a small quantity of iodine, then acetone and a piece of phosphorus, and shaking up the mixture with water, after gently heating it. Its composition is probably C^6H^5I. (Kane.)

Chloride of Mesityl or Hydrochlorate of Mesitylene.

KANE, *Pogg.* 44, 476; also *J. pr. Chem.* 15, 135.

1. Acetone is saturated with hydrochloric acid by passing the gas through it for several days, during which time an abundant absorption takes place, and the resulting dark brown, very acid liquid, is mixed with water, which takes up the hydrochloric acid, and precipitates the chloride of mesityl. This product is then digested with litharge and chloride of calcium; but it still remains contaminated with mesitic ether and acetone. — It is a dark brown liquid, much heavier than water, neutral when recently prepared, but even on the following day, becomes so strongly acid, that it exhales dense fumes of hydrochloric acid. When distilled, it gives off hydrochloric acid and yields a distillate, which, from being mixed with mesitic ether and mesitylene produced in the process, is lighter than water. When distilled with aqueous sulphide of potassium, it yields a yellow liquid which contains a large quantity of undecomposed chloride of mesityl, together with a little mesitic ether, but has a very repulsive odour and gradually deposits sulphur, whence it probably also contains sulphide of mesityl. (Kane.)

2. When a mixture of 1 pt. anhydrous acetone and 2 pts. pentachloride of phosphorus, kept cool by immersing the containing vessel in water, is mixed with four times its bulk of water, and the precipitated pale yellow liquid washed with a small quantity of water, and then dried over chloride of calcium—from which it must be merely decanted, not distilled, because distillation would decompose it—a much purer chloride of mesityl is obtained, mixed however with small quantities of mesitic ether and acetone. (Kane.)

	Prepared by (2).			Kane.
12 C	72·0	....	47·12	47·27
10 H	10 0	....	6·54	6·67
2 Cl	70·8	....	46·34	45·88
$C^{12}H^{10}Cl^2$	152·8	....	100·00	100·00

According to Kane, the formula is C^6H^5Cl.

Chloride of mesityl treated with hydrate of potash, does not yield acetone. (Löwig & Weidmann.)

Mesitic Chloral. $C^6H^4Cl^2O^2$.

LIEBIG (1832) *Ann. Pharm.* 1, 228. — KANE, *J. pr. Chem.* 15, 152.

Formed by passing dry chlorine gas through anhydrous acetone, heating the liquid nearly to the boiling point to facilitate the absorption when it begins to slacken, and separating the resulting oil from the hydrochloric acid which adheres to it, with water. (Liebig.) The oil

is dehydrated by placing it over chloride of calcium and decanting. (Kane.)

Oily liquid, of sp. gr. 1·331. Its odour is faint at first, resembling that of chloroform and Dutch liquid, but after a few seconds becomes so pungent as nearly to take away the senses, and excites a copious flow of tears (Liebig); acts very strongly on the nose and eyes, the effect continuing for some days; produces redness and blisters on the hand, like cantharides; but the wounds which it makes are much more difficult to heal. (Kane).

			Liebig.	Kane.
6 C	36·0	28·39	28·0	28·48
4 H	4·0	3·15	2·8	3·00
2 Cl	70·8	55·84	52·6	56·83
2 O	16·0	12·62	16·6	11·69
$C^6H^4Cl^2O^2$	126·8	100·00	100·0	100·00

The oil boils at about 71°, but during ebullition gives off hydrochloric acid, and becomes dark and opaque. (Kane.) It is decomposed by oil of vitriol and potash with the aid of heat. (Liebig.) When it is mixed with a quantity of potash sufficient to dissolve only half the oil, the undissolved portion does not appear to be altered; but a larger quantity of potash dissolves the oil completely, forming a deep red-brown liquid, which, besides chloride of potassium, contains a peculiar potash-salt, whose acid, *Pteleic acid*, is probably composed of $C^6H^4O^4$; all the salts of this acid are soluble; those of the alkalis are red-brown, and do not reduce the salts of the heavy metals. (Kane.)

Mesityl-hypophosphorous Acid.

When acetone is distilled with phosphorus and iodine, impure iodide of mesityl passes over, and this acid remains in the form of a thick liquid which, on cooling, solidifies in an asbestus-like mass. Dissolves readily in water, producing a bitter and strongly acid liquid, and forms with carbonate of baryta, a soluble and insoluble salt. If the filtrate be then evaporated nearly to dryness, so that it solidifies in a crystalline mass on cooling, and this crystalline mass be freed from iodide of barium by repeated boiling with alcohol, mesityl-hypophosphite of baryta remains in white neutral crystalline grains which take fire when heated, producing a phosphorus-flame and dense fumes of phosphoric acid, and leaving phosphate of bartya mixed with charcoal; when moistened with nitric acid and then heated, they are decomposed with great violence, portions of the mass being scattered about. The crystals, when once formed, take a long time to dissolve completely in water. (Kane, *J. pr. Chem.* 15, 141.)

			Kane.
BaO	76·6	44·02	43·80
P	31·4	18·04	
6 C	36·0	20·70	20·00
6 H	6·0	3·45	3·82
3 O	24·0	13·79	
$BaO,C^6H^6O^2,PO$	174·0	100·00	

Mesitylo-phosphoric Acid.

1 pt. of acetone mixed with 1 pt. of glacial phosphoric acid, becomes heated and yields a dark brown mixture, which when neutralized with an alkali, forms a large quantity of phosphate and a small quantity of mesitylophosphate.

The soda-salt assumes the form of thin rhombic tables, which effloresce in the air, and fuse in their water of crystallization when heated, leaving a soft mass, which, as the heat increases, swells up, blackens, and finally leaves a residue of phosphate of soda. (Kane, *J. pr. Chem.* 15, 144.)

				Kane.
NaO,PO^5	102·6	49·90		48·8
$C^6H^6O^2$	58·0	28·21		
5 Aq	45·0	21·89		20·0
$NaO,C^6H^2O^2,PO^5+5Aq$	205·6	100·00		

Mesitylo-sulphuric Acid.

KANE. *Pogg.* 44, 479; also *J. pr. Chem.* 15, 138.

Obtained by mixing 2 vol. acetone with 1 vol. oil of vitriol, without cooling the mixture artificially; diluting it with water when cold, saturating the acid with carbonate of baryta or lime, and evaporating the filtrate to the crystallizing point. (Kane.)

The *Baryta-salt* decomposed by sulphuric acid yields a liquid, which smells strongly of mesitic ether, contains sulphovinic acid, and when further concentrated by evaporation, gives off sulphurous acid and turns black.

The *Lime-salt* assumes the form of small crystals, which, when heated, give off 7·2 p. c. or 1 At. water (or 2 At. if the salt be supposed to contain 12C). When moistened with nitric acid and heated, it decomposes with slight detonation; does not give off sulphuric acid when more strongly heated, but leaves perfectly neutral sulphate of lime. (Kane.)

	Dehydrated.		Kane.
CaO	28	23·93	23·70
SO^3	40	34·19	
6 C	36	30·77	30·29
5 H	5	4·27	4·40
O	8	6·84	
CaO,SO^3,C^6H^5O	117	100·00	

[Perhaps more correctly, $= 2(CaO,SO^3) + C^{12}H^{10}O^2$. At all events, the salt exhibits a peculiarity not observed in the salts of other conjugated acids, viz. that the quantity of inorganic base contained in it is sufficient to saturate the whole of the sulphuric acid.]

Permesitylo-sulphuric Acid.

KANE. *Pogg.* 44, 479; also *J. pr. Chem.* 15, 138.

One part of acetone is mixed with 2 pts. of oil of vitriol, without cooling, so that the mixture becomes very hot, turns brown, and gives off sulphurous acid; the liquid, when cold, is diluted with water, saturated with carbonate of baryta, lime, or lead, and the filtrate evaporated.

The *Baryta-salt* crystallizes in small pearly tables, turns brown when heated, and leaves 78·4 per cent. of neutral sulphate of baryta. Heated with sulphuric acid, it behaves like mesitylosulphate of baryta.

The *Lime-salt* crystallizes in deliquescent granules and small prisms; may be deprived of its 1 At. water of crystallization without blackening, but blackens and takes fire at a stronger heat, and leaves a slightly alkaline residue, without giving off sulphuric acid. The salt moistened with nitric acid decomposes quite quietly when heated. (Kane.)

	Crystallized.			Kane.
2 CaO,SO^3	136	....	70·10	70·50
6 C	36	....	18·56	18·52
6 H	6	....	3·09	3·33
2 O	16	....	8·25	7·65
$2(CaO,SO^3)+C^6H^6O^2$	194	....	100·00	100·00

[By doubling this formula, we obtain $4(CaO,SO^3)+C^{12}H^{10}O^2+2HO$.]

¶ Sulphomesitylo-sulphuric Acid.

HOFMANN. *Chem. Soc. Qu. J.* 2, 113.

Mesitylo-hyposulphuric acid, Mesitylo-sulphuric acid.

Obtained by treating mesitylene with fuming sulphuric acid, whereby a reddish brown liquid is produced, which, when exposed to a moist atmosphere, becomes gradually crystalline. The application of heat must be avoided as it carbonizes the compound, and gives rise to the evolution of sulphurous acid. The brown liquid becomes colourless when diluted with water, and on adding carbonate of lead in excess, a soluble lead-salt is formed, together with insoluble sulphate of lead. The lead-salt of this acid crystallizes in white needles; it is very soluble both in alcohol and in water. (Hofmann.)

	Lead-salt.			Hofmann.
Pb	104	....	34·23	34·05
18 C	108	....	35·68	35·66
11 H	11	....	3·63	3·81
2 S	32	....	10·58	
6 O	48	....	15·88	
$PbO,SO^3,C^{18}\{H^{11}\}\{SO^2\}$	303	....	100·00	

The formula of this salt may also be written $PbO,C^{18}H^{11}S^2O^5$. ¶.

Acechloride of Platinum.

ZEISE (1840). *Pogg.* 51, 6, 155, and 312; also *Ann. Pharm.* 33, 29; also *J. pr. Chem.* 20, 193.

Chloroplatinite of Mesityl.

Preparation. Dry bichloride of platinum is mixed with a small quantity of acetone, sufficient only to form it into a pasty mass; the mixture placed in a stoppered bottle, and left to itself for 40 hours; and the mass, which has then become black-brown, crystalline, and friable, thrown on a filter, separated from the portion which still remains liquid, and repeatedly washed with small quantities of acetone, whereby a black-brown substance is dissolved, and the residue turned yellow. — The filtrate left in a stoppered bottle, deposits, in the course of 24 hours, an additional quantity of acechloride of platinum, which must likewise be washed with acetone. To obtain the rest of the acechloride of platinum from the filtrate (and wash-liquor), the greater part of the acetone is distilled off from it; the thick syrup poured into a basin; the portion remaining in the retort washed out with a little acetone; the whole left to evaporate in a slowly produced vacuum over oil of vitriol and hydrate of potash; and the residual brittle resinous mass pulverized and washed with acetone, which leaves the acechloride of platinum tolerably pure.

All the acechloride of platinum thus obtained is still contaminated with a body which is insoluble in acetone free from acid. It must, therefore, be dissolved in warm acetone contained in a long-necked flask, and the warm solution filtered from this body into a wide-necked bottle, which is then to be closed: pure acechloride of platinum then separates as the liquid cools. As, however, acechloride of platinum is much more soluble in hot than in cold acetone, the purification may also be effected by immediately distilling the hot-filtered solution nearly to dryness, and freeing the residue from the brown substance by washing with acetone. In this manner, 100 pts. of bichloride of platinum yield about 20 parts of acechloride.

Crystallized; dried in vacuo over oil of vitriol.				Zeise.
6 C	36·0	....	19·63	19·43
5 H	5·0	....	2·73	2·90
Pt	99·0	....	53·98	53·59
Cl	35·4	....	19·30	19·10
O	8·0	....	4·36	4·98
C^6H^5Cl,PtO	183·4	....	100·00	100·00

$= C^6H^5O,PtCl = C^6H^4,HO,PtCl$. (Zeise.)

Decompositions. 1. Acechloride of platinum heated in the oil-bath, sustains without decomposition a temperature of 195°; from 200° to 203°, it turns black and gives off a sour pungent odour; at 215°, it begins to give off gas, which escapes very abundantly at 240°, and consists of a mixture of hydrochloric acid and a combustible gas, with a trace of carbonic acid; up to 300°, the gas is accompanied by a vapour, which condenses to a brown liquid; and there remains a black residue,

which, when heated to redness, gives off a little more of the combustible gas, but no liquid, and is coverted into 60·36 p. c. of bicarbide of platinum (vi, 285). The brown distillate hereby obtained has a peculiar acid odour; fumes in the air in consequence of containing a large quantity of hydrochloric acid; appears to contain acetone; and on addition of water, yields an oil, which rises to the surface, and has a resinous and ethereal odour. The decomposition takes place without fusion or intumescence. When acechloride of platinum is ignited with potash, a residue is likewise formed, containing PtC^2.

2. When acechloride of platinum is immersed in water, both the yellow solution formed at first and the undissolved portion turn brown in a few hours at ordinary temperatures, and immediately on the application of heat. If the liquid be continuously boiled, the water renewed as it evaporates, the solution becomes colourless, and the residue is converted into 58·38 per cent. of a black powder, consisting of aceplatinous oxide.

[If we suppose that aceplatinous oxide$=C^2PtO$, and that hydrochloric ether is produced simultaneously with it, the equation is $C^6H^5PtClO = C^2PtO + C^4H^5Cl$; and consequently, 183·4 pts. of acechloride of platinum must yield 109 pts. of aceplatinous oxide$=100:59·4$, which agrees well enough with Zeise's experiment. This splitting-up of an acetone-compound into a compound of the ethyl-series and one of the methyl-series, is favourable to Chancel's theory of the constitution of acetone.]

3. Acechloride of platinum is decomposed when heated with potash, soda, baryta, or lime, either in the dry or in the humid way. It dissolves slowly in cold potash, forming a brown solution, which indicates a commencement of decomposition. Mixed with a solution of hydrate of potash in 99 per cent. alcohol, it forms a brown pasty mass, which turns black when heated in a retort; and after $\frac{1}{4}$ of the alcohol has passed over, is found to be converted into a black powder, surmounted by a brownish yellow liquid. If the distillation be continued with fresh portions of alcohol, a distillate smelling of hydrochloric ether is finally obtained, and the black powder, surmounted by an almost decolorized liquid, presents the characters of aceplatinous oxide, though with a few peculiar characters.

4. Acechloride of platinum stirred up with a small quantity of aqueous ammonia, dissolves partially, forming first a yellow, then a red-brown alkaline liquid which smells of acetone. This liquid boiled in the retort with the undissolved reddish powder (during which process, thin streams of an ethereal liquid appear in the neck of the retort) dissolves completely, forming a brownish yellow liquid, which, however, if the boiling be continued, becomes darker and deposits a small quantity of blackish powder. When separated from this powder by filtration, and evaporated in vacuo over oil of vitriol, it dries up to a dark brown, brittle mass, which dissolves but partially and sparingly in alcohol. — When dry ammoniacal gas is passed through a solution of acechloride of platinum in acetone, a light yellow powder separates, probably consisting of acechloroplatinate of ammonia, which, if the passage of the gas be continued, is redissolved and forms a clear brownish yellow liquid, in consequence of the formation of an oil, which increases the solvent power of the acetone on the acechloroplatinate of ammonia. (If the solution thus formed be mixed with a fresh solution of acechloride of platinum in acetone, the former precipitate is reproduced). On distilling this clear brown liquid, acetone

first passes over together with ammonia; then a colourless distillate, which becomes milky when mixed with water; then, at the temperature of a chloride of calcium bath, a yellowish liquid, which on addition of water, yields an oil that rises to the surface; and lastly, at a still higher temperature, a thick, brownish yellow liquid from which water likewise separates a large quantity of oil. The honey-yellow, viscid residue in the retort deposits on cooling, red-brown granules of *acechloroplatinate of ammonia*, which remains behind after the red-brown syrupy mother-liquid has been removed by means of ether or acetone. The wash-liquid thus obtained, if mixed with water after the greater part of the ether or acetone has been distilled off, yields a large additional quantity of the above-mentioned oil, which, however, if acetone be present, remains dissolved in considerable quantity in the watery liquid. This oil is slightly volatile, has an alkaline reaction, is difficult to set on fire, and burns with a smoky flame. — Acechloride of platinum dissolved in 98 per cent alcohol saturated with ammoniacal gas, yields at first merely a solution of acechloroplatinate of ammonia precipitable by ether; but soon (probably on the addition of more ammoniacal alcohol), there is formed, besides the soluble acechloroplatinate of ammonia, a dark red body which remains undissolved; but no oil is formed when alcohol is used. The dark red body is permanent in the air, but decomposes when strongly heated, yielding a considerable quantity of sublimed sal-ammoniac and a small quantity of colourless distillate which smells of acetone, and leaving a black substance which burns in the air and leaves metallic platinum. The dark red body is easily set on fire in the air, and burns with a strongly luminous flame tinged with green. It blackens when boiled with water, but does not dissolve in it. It is scarcely soluble in cold hydrochloric acid, but dissolves completely in that acid at a boiling heat, forming a yellow solution. It is insoluble in ether; dissolves sparingly in boiling alcohol; somewhat more abundantly and with yellow colour, in acetone.

5. Phosphorus immersed in the yellow solution of acechloride of platinum in acetone, immediately becomes covered with a black coating, the liquid acquiring first a dark brown, then in half an hour a black-brown colour, and finally losing all its colour and yielding a red-brown, muddy deposit.

6. Acechloride of platinum dissolved in acetone immediately forms with a mixture of acetone and aqueous nitrate of silver, a yellow precipitate, which in a few minutes changes to black-brown, the liquid remaining turbid even after long standing.

7. The solution of acechloride of platinum in acetone covers metallic copper in six hours with a black crust; if a small quantity of hydrochloric acid be added, this effect takes place immediately, and is attended with evolution of gas. With mercury it first forms an amalgam, but after standing for some time, deposits a black powder, whereupon the mercury partly recovers its fluidity.

Combinations. — Acechloride of platinum dissolves sparingly in *water*, forming a yellow solution, which changes by gradual decomposition to brown.

Hydrochloric acid, even when concentrated, does not dissolve it without the aid of heat; but solution then takes place without decomposition.

Acechloroplatinate of Ammonia. — 1. Formed by passing dry ammoniacal gas over dry, finely pounded acechloride of platinum, the colour of which is not thereby altered. The compound yields a large quantity of sal-ammoniac by dry distillation. It dissolves for the most part in water and alcohol, and sparingly in acetone; its aqueous solution is not decomposed by boiling.

2. When ammoniacal gas is passed through a solution of acechloride of platinum in acetone, the same compound is formed and separates at first, but afterwards redissolves in the acetone through the medium of the oil which forms at the same time; but when evaporated, at last in the chloride of calcium bath, it again separates in the granular form, and when the liquid is completely cooled, may be separated from the thick brown liquid by means of ether or acetone. (*vid. sup.*) The residue is yellow, and becomes brown and moist at the edges when exposed to the air, more probably by oxidation than by absorption of water. It decomposes at high temperatures, and burns away with flame when strongly heated in the air. It dissolves very readily in water, forming a brownish yellow liquid, which has a strong alkaline reaction, but does not smell of ammonia; may be evaporated to dryness without decomposing; and when heated with a small quantity of potash, forms a small quantity of yellowish precipitate, which on the addition of more potash, redissolves with copious evolution of ammonia. It dissolves very abundantly in alcohol, and is precipitated from the solution by ether. The solution has a very strong alkaline reaction, and when mixed with an alcoholic solution of bichloride of platinum, forms a copious greenish yellow precipitate, which is rich in carbon; if ether be then added to the filtrate, a small quantity of light yellow precipitate is formed, which, after being dried on the filter, is quickly converted by exposure to the air, into a brown tar. It dissolves sparingly in acetone at ordinary temperatures, more abundantly at a boiling heat; the undissolved portion is undistinguishable from that which dissolves.

3. Acechloride of platinum is dissolved in ammoniacal alcohol (p. 33) in such proportion that the red-brown liquid still remains slightly alkaline; the solution filtered from the small quantity of undissolved substance; the acechloroplatinate of ammonia precipitated from the filtrate by agitation with a large quantity of ether, in large yellow flakes; and these flakes collected on a filter (the filtrate, if a sufficient quantity of ether has been added, is colourless, and retains scarcely anything in solution), and dried in vacuo. This process yields acechloroplatinate of ammonia in the form of a light yellow substance — brownish yellow and gummy at the edges only—which dissolves very readily in water, but in alcohol only partially, and much more slowly than the substance obtained by (2).

Acechloride of platinum dissolves sparingly in *Ether*, more readily in alcohol, especially in hot alcohol, from which it crystallizes on cooling; and still more readily, in the proportion of 1 : 30, in acetone, which solution does not exhibit any acid reaction till mixed with water. (Zeise.)

Platinum-resin.

ZEISE. *Ann. Pharm.* 33, 34, and 66; also *J. pr. Chem.* 20, 197, and 223.

A solution of 1 pt. bichloride of platinum in 10 pts. acetone is distilled, after it has become dark; the remaining syrup treated with water, as long as the water continues to be coloured by it. The residue, consisting of *crude platinum-resin*, may be dried in vacuo over lime or over oil of vitriol and hydrate of potash.

Crude platinum-resin is black-brown, unctuous, brittle at ordinary temperatures, but when gently heated, soft, tenacious, and capable of being drawn out into threads.

When subjected to dry distillation, it gives off gas from 200° upwards; swells up at 230° to forty times its original bulk; shrinks together again at 270°, yielding at the same time a large quantity of gas, and a distillate, yellowish at first, then brownish, somewhat thick, smelling strongly of hydrochloric acid, and resembling that which is obtained in the distillation of acechloride of platinum. From 300° to incipient redness, it continues to yield a large quantity of gas and distillate. The brittle carbonaceous residue, which has a fatty lustre, likewise gives off, when heated to whiteness in a porcelain retort, a large quantity of gas free from hydrochloric acid and burning with a strongly luminous flame. This residue still amounts to 42·85 per cent of the dry crude platinum-resin, and leaves, when ignited in the air, 45·62 per cent of its weight of platinum, whence it must contain 19 or 20 At. carbon to 1 At. platinum. According to this result, crude platinum-resin contains 19·55 per cent of platinum. — If the platinum-resin be mixed with hydrate of potash previous to distillation, it yields, between 200° and 300°, without giving off any appreciable quantity of gas, a pale yellow, turbid, thickish distillate having a resinous and ethereal odour; and from 300° up to a red heat, a distillate of similar character, excepting that it becomes continually browner and thicker, ultimately solidifies as it cools, becomes continually less combustible, and burns with a more smoky flame. — The dry distillation of platinum-resin with powdered quicklime takes place without intumescence.

Crude platinum-resin is a mixture of several products of decomposition. If it be treated, at ordinary temperatures, so long as each of the successive liquids becomes coloured, first with spirit of 80, then of 93 per cent, then with absolute alcohol, then with ether, and lastly with acetone, first cold and then boiling, a black residue is left, and various solutions are obtained, all having a dark brown colour so strong as to render them opaque, and containing more or less acechloride of platinum. The alcoholic extracts are partly precipitable by water, yielding greyish yellow precipitates; the ethereal solution mixed with alcohol yields greyish black, dark brown, and black precipitates; and the acetone solution is precipitable by ether. These solutions all yield by evaporation dark amorphous residues: that which remains from the alcoholic solutions dissolves readily in potash-ley; the residue of the solutions in ether or acetone, sparingly or not at all. All these residues, when subjected to

dry distillation (those only from the alcoholic extracts swelling up) yield a gas, part of which is highly combustible, a chlorinated distillate, consisting of a colourless and a yellow or brown liquid mixed together, and a residue of carbide of platinum.

When dry ammoniacal gas is passed through a very dark brown alcoholic solution of crude platinum-resin, till the liquid becomes slightly alkaline, a large quantity of *yellow crystalline* powder is precipitated, resembling chloroplatinate of ammonium. This precipitate, after being washed, first with weak spirit till the little crystals of sal-ammoniac mixed with it are dissolved out and the wash-liquid no longer forms a cloud in silver-solution,—and afterwards with spirit of 98 per cent, presents the appearance of a yellow crystalline powder. Subjected to dry distillation, it yields at high temperatures a sublimate of sal-ammoniac, a colourless distillate, and a carbonaceous residue which leaves platinum when burned. It dissolves to a certain extent in alcohol, forming a yellow solution, and is not decomposed when this solution is boiled or evaporated. The solution does not precipitate bichloride of platinum or nitrate of silver; but, when heated with the latter, it becomes clouded by a red-brown precipitate, which, on addition of nitric acid, becomes colourless and is converted into chloride of silver. The alcoholic solution likewise yields a precipitate of chloride of silver when mixed with nitric acid and then with nitrate of silver, the precipitate being formed gradually at ordinary temperatures, and more quickly on the application of heat. The yellow crystalline powder dissolves very sparingly in acetone, but more freely when sal-ammoniac is present.

If the alcoholic liquid filtered from the yellow crystalline powder be distilled till two-thirds have passed over, the residue deposits brown crystals which may be collected on a filter; they are much more soluble in alcohol than the yellow crystalline powder.—If the washing with alcohol be continued till the greater part is dissolved, the residue when dissolved in fresh alcohol gives a strong precipitate with nitrate of silver, but does not produce the brown colour when heated.

The dark brown mother-liquor run off from these brown crystals, distilled to dryness in the chloride of calcium bath, yields a residue which when treated with ether, leaves an insoluble *black crystalline body*. This substance treated with boiling spirit of 98 per cent, yields a yellowish brown liquid, which, when evaporated, leaves a brown residue partly soluble with yellowish-brown colour in water, and leaving a blackish residue. The yellowish brown alcoholic solution is not precipitated by cold water, but when boiled with water till the alcohol evaporates, it yields a brown turbid liquid. This liquid yields a brownish filtrate which precipitates a solution of nitrate of silver, but not with red-brown colour, and deposits red-brown flakes, both with hydrochloric acid and with potash, the solution in the latter case being decolorized; these flakes are produced in particular abundance on boiling the liquid, in which case, if potash be used, a trace of ammonia is given off.

The dark brown ethereal liquid filtered from the black crystalline body, leaves, when evaporated in vacuo over oil of vitriol, first a red-brown, transparent syrup, then a red-brown, solid residue. The alcoholic solution of this residue neutralized or supersaturated with ammonia, deposits a small additional quantity of the yellow crystalline powder, a portion of which still remains when the liquid is evaporated to dryness in vacuo, and the residue exhausted with ether; this red-brown ethereal solution leaves on evaporation, a residue consisting of *indifferent platinum-*

resin. This substance dissolves completely with red-brown colour, in ether and alcohol, and is precipitated from the latter solution by water in large brown flakes. It is perfectly neutral. By dry distillation it yields an acid suffocating vapour, a yellow, resinous sublimate (no sal-ammoniac), and a carbonaceous residue. It burns in the flame of a spirit-lamp with a bright but very sooty flame, leaving a small quantity of platinum. Its alcoholic solution is somewhat darkened by addition of hydrochloric acid, and when mixed with nitrate of silver and left to stand for some time, yields a copious greyish yellow precipitate.

The extract of crude platinum-resin prepared with acetone likewise yields a yellow crystalline precipitate with ammonia. (Zeise.)

Aceplatinous Oxide.

ZEISE. *Ann. Pharm.* 33, 54; *J. pr. Chem.* 20, 213.

Precipitated in the form of a black powder on boiling acechloride of platinum with water; also in considerable quantity on boiling the dark brown liquid from which acechloride of platinum has been deposited (p. 10).

Coal-black powder, containing 92·01 per cent of platinum. — [The formula C^2PtO requires 90·82 p.c. platinum.]

Takes fire when heated for some little time, with brisk decrepitation and tolerably loud report, often on merely admitting the air to it after it has dried in vacuo, inasmuch as it then absorbs the air and becomes heated. A thin layer of the powder placed on paper moistened with alcohol, takes fire in the same manner and generally sets fire to the alcohol. With ether or acetone no such effect is produced. Nitric acid does not exert much action on this substance, but aqua-regia when digested with it for some time, dissolves a portion with yellowish colour, leaving a residue of the same colour. — Strong hydrochloric acid digested with the powder dissolves but a small portion of it, forming a red-brown solution. — Acetone in the course of 24 hours dissolves a small portion of it, acquiring a brownish colour.

Aceplatinous oxide prepared by means of alcoholic potash is likewise a coal-black powder, free from metallic particles, and exhibiting the above reactions with alcohol. But it dissolves readily and completely in aqua-regia, and is very little attacked by hydrochloric acid. (Zeise.)

¶ Acetonic Acid. $C^8H^8O^6 = HO,C^8H^7O^5$.

STÄDELER. *Chem. Gaz.* 1853, 341.

Formed from acetone in the same manner as formobenzoilic acid from oil of bitter almonds. Crystallizes in prisms; has a strongly acid taste and reaction; dissolves readily in water, alcohol, and ether, and fuses when heated, into a colourless oily liquid, which again solidifies in the crystalline form on cooling. By fusion with an excess of hydrate of potash, it yields acetone. When heated with strong sulphuric acid, it is decomposed with abundant evolution of gas. Forms crystallizable salts

with bases. The *zinc-salt*, $C^8H^7ZnO^5$, closely resembles lactate of zinc, but dissolves sparingly in water even at a boiling heat; it is insoluble in alcohol and ether; gives off its water a little above 100°. — The *baryta-salt*, $C^8H^7BaO^6$, dissolves readily in water and in alcohol, but is insoluble in ether. Crystallizes only from a very strong solution, forming small white prisms, or long fibrous, satin-like, crystalline masses, which lose their water of crystallization even in vacuo. — On adding nitrate of silver to a tolerably strong solution of the acid neutralized with ammonia, metallic silver is slowly deposited in dark flakes.¶

Acetal. $C^{12}H^{14}O^4$.

Liebig. *Ann. Pharm.* 5, 25; also *Pogg.* 27, 605. — *Ann. Pharm.* 14, 156.
Stas. *N. Ann. Chim. Phys.* 19, 146; also *J. pr. Chem.* 40, 340.

Heavy Oxygen-ether, Schwerer Sauerstoffäther. — For the history of this compound, *vid.* VIII, 274.

Formation. By the imperfect combustion of alcohol in contact with platinum-black. (Döbereiner.) — 2. In the decomposition of alcohol by chlorine, so long as no substitution-products are formed, acetal is the principal product (Stas.):

$$3C^4H^6O^2 + 2Cl = C^{12}H^{14}O^4 + 2HCl + 2HO.$$

[This formation of acetal from hydrated alcohol appears to precede the formation of aldehyde (VIII, 214):

$$C^{12}H^{14}O^4 + 2HO + 4Cl = 3C^4H^4O^2 + 4HCl.]$$

Preparation. A number of watch-glasses containing moist platinum-black are placed on a stand above a quantity of spirit of 60 to 80 per cent. contained in a shallow dish; the whole covered with a bell-jar so arranged so to allow a certain access of air; the liquid, which becomes acid in two or three weeks, and then consists of water, alcohol, acetic acid, acetic ether, aldehyde, and acetal, neutralized with chalk, and distilled; and the distillate saturated with chloride of calcium, above the solution of which there rises a thin mixture of acetic ether, aldehyde, and acetal. If this liquid be distilled, aldehyde and acetic ether pass over first; but at 94° to 95°, at which point the receiver should be changed, the chief product is acetal, which must be purified by repeated rectification, the portion which goes over from 94° to 95° being always collected in a separate receiver. It may be freed from the remainder of the aldehyde by passing ammoniacal gas through it and washing with water; but to purify it completely from acetic ether is more difficult. If the rectified product be repeatedly digested with chloride of calcium, a white pulverulent precipitate is deposited after all the water and alcohol have been removed, probably consisting of the compound of chloride of calcium and acetic ether already described (VIII, 499). — If the distillate obtained after neutralizing with chalk be repeatedly treated with chloride of calcium, till that substance is no longer moistened; the liquid then distilled; and the portion which passes over at 94° collected apart; this portion exhibits a boiling-point rising from 88° to 110°, in consequence of the admixture of a large quantity of acetic ether; hence if the portion

which passes over at 88° be shaken up with strong potash, it diminishes in a few hours to less than half its bulk, in consequence of the formation of alcohol and acetate of potash. (Stas.)

2. Pieces of pumice-stone, washed and ignited, are moistened with nearly absolute alcohol, and placed on the bottom of a short and wide-necked glass globe of 40 or 50 litres capacity; a number of capsules, as many as the globe will hold, each covered with a thin layer of platinum-black, are placed on the pumice-stones; and the globe, covered with a well fitting glass plate, is set aside at a temperature of at least 20°, till all the alcohol has become acid. One or two litres of 60 per cent alcohol are then poured upon the bottom of the globe, the quantity being however not sufficient to cover the pumice-stones completely; the globe covered and left for two or three weeks at 20°, the air being frequently renewed; the thickish liquid under the pumice-stones drawn off and replaced by an equal quantity of fresh alcohol; and this process repeated till several litres of thickish acid liquid have been thus obtained. This liquid is either neutralized with carbonate of potash and then saturated with chloride of calcium, or neutralized with carbonate of potash and saturated with dry acetate of potash, or merely saturated with actetate of potash without previous neutralization, — after which, it is distilled into a well cooled receiver, till a fourth has passed over. On saturating this distillate with chloride of calcium, a pungent mixture of aldehyde, acetal, acetic ether, and alcohol separates out, and may be removed with a pipette. A further quantity of this mixture may be obtained by adding water to the remaining chloride of calcium solution, as long as any of it continues to separate; and the dilute chloride of calcium solution yields a little more by distillation. Chloride of calcium is then added to the alcoholic mixture, as long as it is thereby liquefied; this mixture decanted from the chloride of calcium solution, and distilled without boiling, till the distillate no longer reduces an ammoniacal solution of acetate of silver, that is to say, till the residue is free from aldehyde; the distillate mixed with a very large excess of strong potash, set aside, and frequently shaken, to decompose all the acetic ether; the decanted liquid washed once or twice with an equal volume of water to remove the alcohol; then digested with chloride of calcium, and distilled from small retorts in contact with platinum wire or metallic mercury. (Stas.)

3. Chlorine gas is passed through 80 per cent alcohol cooled to 10° or 15°, till substitution-products are formed, which may be known by a portion of the alcohol becoming turbid on the addition of water. One-fourth of the strongly acid liquid is then distilled off; the distillate neutralized with chalk; one-fourth again distilled off; the distillate treated with chloride of calcium, whereupon a mixture of alcohol, acetic ether, aldehyde and acetal rises to the surface; this stratum of liquid freed as completely as possible from alcohol and ether by means of chloride of calcium; and purified in the same manner as in (2). (Stas).

Properties.—Transparent colourless liquid as thin as ether (Liebig); much less fluid (Stas). Sp. gr. 0·823 at 20° (Liebig); 0·821 at 22·4° (Stas). Boiling point 95·2° at 27″ 9‴ (Liebig); 104° to 106° at 0·768 met. (Stas). Vapour-density 4·141 (Stas). Smells like heavy hydrochloric ether (Liebig); has a peculiar agreeable odour, and a refreshing taste, with an after-taste like that of hazel-nuts (Stas).

			Liebig.	Stas.		Vol.	Density.
12 C	72	61·02	59·59	60·70	C-vapour	12	4·9920
14 H	14	11·86	11·86	11·94	H-gas	14	0·9702
4 O	32	27·12	28·75	27·36	O-gas	2	2·2186
$C^{12}H^{14}O^4$	118	100·00	100·00	100·00	Acetal-vapour	2	8·1808
						1	4·0904

Liebig, from the analysis of his acetal (which was probably not quite free from acetic ether), deduces the formula $C^8H^9O^3$. — Acetal is in the ethylene-series, what methylal, $C^6H^8O^4$ (VII, 310), is in the methylene-series. — It might be regarded as a conjugated compound of 2 At. ether with 1 At. aldehyde $= 2C^4H^5O + C^4H^4O^2 = C^{12}H^{14}O^4$; but its behaviour with alkalis and silver-solutions renders the presence of aldehyde improbable. (Stas.) [Or it is a conjugated compound of 1 At. acetic ether with 4 At. alcohol *minus* 4 At. water:

$$C^8H^8O^4 + 4C^4H^6O^2 = C^{24}H^{28}O^8 + 4HO$$

(see the observations on methylal, VII, 262 to 263); but the behaviour of the compound with alcohol is unfavourable also to this supposition.]

Decompositions. Acetal is doubtless inflammable. — It is permanent when alone, both in moist and in dry air; but in contact with air and platinum-black, it is quickly converted into aldehyde, and then into strong acetic acid (Stas):

$$C^{12}H^{14}O^4 + 4O = 3C^4H^4O^2 + 2HO.$$

The conversion into acetic acid was previously mentioned by Liebig. — Chlorine abstracts hydrogen and forms chlorine-products not yet examined. (Stas.) — Dilute nitric acid first forms aldehyde, then acetic acid; chromic acid yields only the latter. (Stas.) — Oil of vitriol dissolves acetal, and decomposes it with blackening. (Stas.) — Acetal, either alone or dissolved in alchhol, does not reduce silver-salts (Liebig), not even acetate of of silver mixed with ammonia. (Stas.) — When kept from contact of air, it is not decomposed by strong potash or soda-ley, by hydrate of potash or soda, or by hydrate of lime, even with the aid of heat. (Stas.) — Its mixture with alcoholic potash assumes a brown colour when exposed to the air, from formation of aldehyde-resin, the colour proceeding from top to bottom, and becoming continually darker; but when heated out of contact of air, it remains unaltered, acquiring however an unpleasant soapy odour; if it be then poured into a wide vessel containing air, it absorbs oxygen gas. (Liebig.)

Combinations. Acetal dissolves in 6 or 7 parts of *Water* (Liebig); at 25°, it requires 18 times its volume of water to dissolve it, its solubility increasing as the temperature rises (Stas); chloride of calcium and most salts that are soluble in water, separate acetal from water. (Stas.)

Acetal mixes with *Alcohol* and *Ether* in all proportions. (Liebig.) From its combination with alcohol, it cannot be separated by chloride of calcium, unless water be likewise added. (Stas.)

Lignone.

L. Gmelin. *Handb.* Aufl. 3, 2, 344. — *Ann. Pharm.* 25, 47.
Liebig. *Ann. Pharm.* 5, 32; also *Pogg.* 27, 613.
Löwig. *Pogg.* 42, 404. The properties there attributed to wood-spirit, really belong, according to *J. pr. Chem.* 20, 435, to Lignone.
Weidmann & Schweizer. *Pogg.* 43, 593; 49, 135, 293 and 323; 50, 265; also *J. pr. Chem.* 23, 14. — The whole together: *J. pr. Chem.* 23, 14.

Xylite (Weidmann & Schweizer); *Formosal* (Kane). — For the history of this substance, *vid.* VII, 258. Reichenbach (*Schw.* 69, 241) maintained that lignone is a mixture of alcohol and his *mesite*, which latter he regarded as acetone (p. 52). Liebig (*Ann. Pharm.* 10, 315) pointed out the incorrectness of this view, showing that the properties of a mixture of alcohol and acetone are very different from those of lignone. Weidmann and Schweizer have made the most elaborate investigation of lignone, and examined many of its products of decomposition.

Lignone is formed in the dry distillation of wood, and occurs in crude wood-vinegar together with other spirituous liquids, viz., wood-spirit, acetone, aldehyde, Reichenbach's mesite, (methylic acetate?) and Weidmann & Schweizer's mesite. The wood-spirit and methylic acetate generally predominate, the latter being resolved, when the crude wood-spirit is distilled over lime, into methylic alcohol and acetate of lime (VII. 259). In crude wood-spirit from Wattwyl, Gmelin found a large quantity of lignone, and in samples from a wood-vinegar manufactory at Zürich, Weidmann & Schweizer found in one instance nearly pure methylic alcohol, in another, chiefly lignone.

Preparation. 1. The first portions of distillate obtained in the distillation of crude wood-vinegar are freed from the empyreumatic oil which floats on the surface, and repeatedly rectified over lime, the more fixed portion being each time thrown aside. The resulting distillate, consisting of wood-spirit, lignone, W. & Schw.'s mesite, and a small quantity of empyreumatic oil [and a little water] is saturated with chloride of calcium; this solution distilled in the water-bath, without adding fresh chloride of calcium, which would retain a portion of the lignone as well as the wood-spirit; and, the distillate, consisting of lignone, mesite, empyreumatic oil, and a small residual quantity of wood-spirit, freed from this residue by repeated distillation, in which process a small quantity of lignone is also retained by the chloride of calcium. The liquid is then distilled alone till the distillate, when mixed with water, becomes turbid from the presence of empyreumatic oil; the distillate mixed with finely pounded chloride of calcium, with which it forms a tumefied mass and a liquid, containing many impurities dissolved in the lignone; the liquid after a few days allowed to run off by a filter; and the residue on the filter, which contains chloride of calcium in combination with pure lignone, distilled in the water-bath, whereupon the latter passes over. (Weidmann & Schweizer.)

Pure lignone treated with hydrate of potash should instantly yield white shining laminæ of a peculiar potash-salt; if this effect takes place after some time only, the lignone contains wood-spirit which retains the salt in solution, so that it does not separate till a larger quantity of potash-hydrate is added, which at the same time occasions a further decomposition of the lignone. — If the lignone contains mesite, even in small quantity, it is immediately turned brown by potash, even during the separation of the above-mentioned potash-salt.

2. Pure wood-spirit is rectified; the distillate saturated with chloride

of calcium; the empyreumatic oil which separates from the solution removed; the remaining liquid distilled in the water-bath; and the first portion which passes over collected separately, because it is only the latter portions which contain the purer lignone, which must then be freed from water by rectifying it several times over chloride of calcium, till the boiling point becomes constant.

3. Crude wood-spirit, after being mechanically freed from empyreumatic oil, is rectified several times over milk of lime, then repeatedly with an equal quantity of water, the oil which separates on the addition of water being each time set aside, and the distillation interrupted as soon as all the alcoholic portion has passed over. The product is then distilled several times over small quantities of chloride of lime, to resinize the remaining portion of oil and render it more fixed [which however may be injurious from the action which chloride of lime is apt to exert upon lignone]; and lastly the spirit is freed from water and methyl-alcohol by repeated distillation in the water-bath, first over a small quantity, and then over a large quantity of chloride of calcium. The lignone thus purified still however retains a trace of empyreumatic oil, which may be detected by the odour. (Gm.)

Properties. Thin, transparent, colourless liquid. Sp. gr. 0·816 (Weidm. & Schweizer), 0·804 at 18° (Liebig), 0·797 (Löwig), 0·836 at 12·5° (Gm.) Boils at 61·5°. According to Löwig and to Wiedmann & Schweizer, it boils at 60° with the barometer at 28″ (Liebig); 61·25° at 27″ 6‴ (Gm). Vapour density = 2·177 (W. & Schw.); 1·824 (Kane). Has a pleasant ethereal odour (W & Schw.); penetrating and ethereal (Liebig); somewhat like that of acetic ether (Gm.) Its taste is burning (W. & Schw.); biting and aromatic (Liebig, Gm.) Does not redden litmus.

Calculations.

	At.		*a.*	Vol.	Density.	At.		*b.*	Vol.	Density.
C	8	48	53·33	8	3·3280	12	72	53·73	12	4·9920
H	10	10	11·11	10	0·6930	14	14	10·45	14	0·9702
O	4	32	35·56	2	2·2186	6	48	35·82	3	3·3279
		90	100·00		6·2396		134	100·00	4	9·2901
									1	2·3225

	At.		*c.*	Vol.	Density.	At.		*d.*	Vol.	Density.
C	12	72	58·06	12	4·9920	10	60	58·82	10	4·1600
H	12	12	9·68	12	0·8316	10	10	9·81	10	0·6930
O	5	40	32·26	2½	2·7732	4	32	31·37	2	2·2186
		124	100·00	4	8·5968		102	100·00	4	7·0716
				1	2·1492				1	1·7679

Analyses.

	W. & Schw.	Liebig.		Kane.	L. Gmelin.			
		a.	*b.*		*a.*	*b.*	*c.*	*d.*
C	58·50	48·11	54·75	54·88	53·25	54·77	55·37	57·71
H	10·04	11·81	11·11	11·27	10·62	10·12	9·83	10·34
O	31·46	40·08	34·14	33·85	36·13	35·11	34·80	31·95
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

The lignone *a* analyzed by Liebig had been freed from water and alcohol by two, and *b* by four rectifications over chloride of calcium. — Kane (*Ann. Pharm.* 19, 180,) examined a residue of Liebig's lignone. — The lignone *a* examined by Gmelin was obtained by (3), had a density 0·836, and boiled at 61·25°; *b* was purified by several rectifications *a* over chloride of calcium, and *c* by one more; it had a density of 43; and boiled at 59°. The lignone *d* was obtained by repeated distil-

lation of Parisian wood-spirit in the water-bath, over large quantities of chloride of calcium; but its odour, and its boiling point, which was about 58·75°, indicated the presence of acetone.

Both the analyses and the determinations of vapour-density, differ too much from one another to allow of the deduction of an exact formula for lignone. If a sample of wood-vinegar contains but a small quantity of acetone, this impurity will, in all probability, remain attached to the lignone prepared by the several processes above detailed. If we attempt to dehydrate the lignone, as much as possible, by repeated distillation in the water-bath over chloride of calcium, a portion of the lignone is always retained by the chloride of calcium, while all the acetone, which does not appear to unite with the chloride of calcium, passes over; hence the lignone must become continually richer in acetone, and therefore also in carbon. But, admitting the validity of this explanation, with regard to Gmelin's analysis of lignone *d*, it must still be doubtful with respect to Weidmann & Schweizer's analysis, inasmuch as the boiling point found by these chemists was by no means below that which Liebig and others had observed in samples of lignone containing less carbon, whereas the presence of acetone, which boils at 56°, would have lowered the boiling point of the lignone. Can the difference be due to the presence of a less volatile compound, similar in other respects to acetone?

Whatever may be the true formula of lignone, it appears to be a conjugated compound, perhaps of higher order, and containing, as Weidmann & Schweizer suppose, a compound of the methylene series and another of the ethylene series. For its boiling point is too low to allow it to be regarded as a primary compound of a nucleus, containing 8 or more atoms of carbon; moreover, according to Weidmann & Schweizer, it yields, when decomposed in various ways, on the one hand, wood-spirit, formic acid, sulphate of methyl, and sulphomethylic acid, and on the other, aldehyde, acetic acid, and acetic ether.

Weidmann & Schweizer assign to lignone the formula $C^6H^6O^{2\frac{1}{2}}$, according to which, it is a compound ether of the third class (VII, 190), *viz.*, *hypoacetylite of methyl*$=C^2H^3O,C^4H^3O^{1\frac{1}{2}}$. But this *hypoacetylous acid* (or *xylitic acid*, as Weidmann & Schweizer call it), which, in the hypothetical anhydrous state, would be composed of $C^4H^3O^{1\frac{1}{2}}$ is unknown, and indeed impossible, on account of the division of the atom. —At all events, we should have to double the formula of lignone and make it $C^{12}H^{12}O^5$, in order to get rid of the half-atom; but even then, the formula is improbable by reason of the uneven number of atoms which it exhibits. Equally improbable are the highly complicated equations by which these chemists seek to explain some of the reactions of lignone, wherein they are driven to admit the existence of acetylous or aldehydic acid ($C^4H^4O^3$, or in the hypothetical anhydrous state, $C^4H^3O^2$), as well as of the above-mentioned hypoacetylous acid.

According to Völckel (*Pogg.* 83, 27, 577; abstr. *Jahresber.* 1851, 498), Weidmann & Schweizer's xylite is a mixture of methylic acetate, acetone, and another substance polymeric with the latter, to which Völckel proposes to transfer the name of xylite. He finds that the liquid obtained by repeatedly treating crude wood-spirit with chloride of calcium and distilling fractionally, varies in boiling point from 55° to 120°. The portion which passes over between 55° and 71°, exhibits the properties of Weidmann & Schweizer's xylite, but does not exhibit a constant boiling point, or yield any definite product by treatment with chloride of calcium. The pure xylite is obtained by repeatedly rectifying the

portion which passes over between 61° and 70°. It is a colourless liquid of peculiar odour and burning taste. Sp. gr. 0·805. It distils over completely between 61° and 62°; mixes in all proportions with water, alcohol, and ether, and is precipitated from its aqueous solution by water or by an alkali. Its formula is $C^{12}H^{12}O^4$. ¶.

Decompositions. 1. Lignone *burns* with a flame which is reddish yellow above and blue below; does not smoke; gives more light than that of alcohol but less than that of ether. (Gm.)

2. Dry *chlorine gas* passed through lignone gives rise to a tolerably strong action and evolution of hydrochloric acid gas, and forms two layers, the lower of which is oily, and continually increases at the expense of the upper. Towards the end of the process, the action must be increased by the application of a gentle heat, after which, the resulting oil (xylitic chloral) may be washed with water, and dehydrated by chloride of calcium, which does not dissolve in it.

This *Xylitic Chloral* contains 29·25 per cent C, 3·51 H, 58·32 Cl and 8·92 O; its formula is therefore $C^{12}H^8Cl^4O^3$. [Probably formed in this manner:

$$C^{12}H^{12}O^5 + 6Cl = C^{12}H^8Cl^4O^3 + 2HO + 2HCl\,?]$$

Xylitic chloral has a very pungent odour, gives off hydrochloric acid when distilled, and yields a distillate of various volatile compounds, while a quantity of solid matter remains behind. When distilled with water, it first passes over undecomposed, then gives off hydrochloric acid, and is converted into another compound. (Weidmann & Schweizer.)

3. Lignone placed in a test-tube with an equal volume of strong *nitric acid*, so as to form a layer above it, becomes heated, and quickly passes into a state of violent intumescence, and is thrown out of the tube by jerks, giving off nitric oxide gas which has an ethereal odour, and leaving a liquid clouded with oily drops, which increase on the addition of water. The yellow watery liquid contains oxalic acid, and turns brown on the addition of ammonia; the oil is yellow and viscid, tastes sweet and aromatic at first, but afterwards sharp and burning, leaving for hours a burning sensation on the tongue. (Gm.)

4. Lignone slowly mixed with an equal volume of *oil of vitriol*, forms a light brown syrup. (Gm.) When quickly mixed with oil of vitriol, it becomes strongly heated, and forms a thick dark brown mixture. Water added to this mixture takes up acetic and sulphomethylic acids, and separates a black-brown oil, consisting of lignone, mesite, xylitic naptha, xylite-oil, and a brown and yellow xylitic resin. With 2 pts. lignone to 1 pt. oil of vitriol only a small quantity of oil consisting chiefly of mesite and xylitic naphtha, separates on the addition of water; — if the liquids are mixed in equal volumes, the products are formed in equal quantities; — with 1 pt. of lignone to 3 pts. of oil of vitriol, the chief products are xylite-oil and xylite-resin. (Weidmann & Schw.) — Lignone distilled with an equal quantity of oil of vitriol gives off sulphurous acid from the first, but in continually increasing quantity. The first products which collect in the receiver are lignone and mesitene, — then two layers of liquid, the lower consisting of aqueous acetic acid, the upper of mesite and methol; lastly, a small quantity of methylic sulphate passes over. — When 1 pt. of lignone is distilled with 4 pts. of oil of vitriol, the mixture froths up strongly, and gives off a large quantity of sulphurous acid, together with acetic acid, acetate of methyl, sulphate of methyl, and a small quantity of mesitene, but no methol. — With 16 pts. oil of vitriol, the distillation takes place quietly, and a very

large quantity of acetic acid is obtained, together with much sulphurous acid and methylic sulphate, very little methylic acetate and no methol. — In all these distillations, a carbonaceous mass remains behind. (Weidmann & Schweizer.) — When 1 pt. of lignone is distilled with 2 pts. of oil of vitriol and 1 pt. of acid oxalate of potash, sulphurous acid is continually evolved; lignone and mesitene pass over first; then oxalate of methyl, acetic acid, and methol; and at last a small quantity of methylic sulphate. (Weidmann & Schweizer.) — According to Völckel, the products obtained by the action of oil of vitriol on lignone, are the same as those produced by excess of caustic potash. (*vid. inf.*)

5. When 2 pts. of lignone are distilled with 2 pts. of *peroxyde of manganese*, 3 pts. of *oil of vitriol*, and 3 pts. of water, lignone passes over first, together with a large quantity of aldehyde, then, till the end of the distillation, water containing formic acid. (Weidmann & Schweizer.)

6. When *hydrate of potash* is gradually added in small pieces to anhydrous lignone, kept from contact with the air, the pieces swell up on being immersed, and in a few minutes white silvery laminæ separate out. If the addition of the potash be discontinued, as soon as the liquid begins to turn brown here and there, and the liquid be then set aside for a while, the crystals, together with the solution, may be decanted from the hydrate of potash at the bottom of the vessel, and thrown on a filter; they must then be left out of contact of air, till the liquid has run through, after which they may be washed with water, and dried in vacuo over oil of vitriol. The hypoacetylite of xylite and potash thus obtained, is greasy to the touch and very deliquescent. Its aqueous solution decomposes in the air, from formation of acetate of potash and separation of lignone. When distilled with dilute sulphuric acid, it yields acetic acid; it dissolves readily in anhydrous wood-spirit, but is nearly insoluble in anhydrous lignone. In the crystalline state, it contains 43·00 p.c. KO, 33·87 C, 4·92 H, and 18·21 O; it is therefore 3KO, 18C, 15H, 7O = 3(KO,$C^4H^3O^{11}$) + (C^2H^3O,$C^4H^3O^{11}$), that is to say, a double salt, in which 3 At. hypoacetylite of potash are united with 1 At. hypoacetylite of methyl (= 1 At. lignone = $C^6H^6O^{21}$). Lastly, since the liquid from which these crystals are deposited contains lignone, the equation for their formation must be:

$$4C^6H^6O^{21} + 3(KO,HO) + 3(KO,C^4H^3O^{11}) + C^6H^6O^{21} + 3C^2H^4O^2.$$

(Weidmann & Schweizer.)

If the quantity of potash-hydrate added to the lignone be larger than is required to form hypoacetylite of xylite and potash, this salt gradually dissolves, and the liquid acquires a brown colour, which increases with the quantity of potash, and the time during which it is left. Water added after some time, throws down a dark brown, oily mixture of mesite, xylitic naphtha, xylite-oil, and brown xylite-resin, which are formed one after the other in the order in which they are here enumerated. For, as the potash continually sets free more wood-spirit from the hypoacetylite of methyl (lignone), the hypoacetylite of potash is by that wood-spirit more and more completely dissolved. This salt, under the simultaneous influence of the free potash, then abstracts oxygen from the hypoacetylous acid of the free lignone, and is thereby converted into acetate of potash; and the [hypothetical] oxide of acetyl, C^4H^3O, produced by this reduction of the hypoacetylous acid, remains in combination with the methylic ether of the lignone, forming mesite ($C^6H^6O^2$):

$$KO,C^4H^3O^{11} + 3C^6H^6O^{21} = KO,C^4H^3O^5 + 3C^6H^6O^2.$$

The mesite thus formed is then reduced by further quantities of acetylite of potash to xylitic naphtha. (Weidmann & Schweizer.)

When lignone is distilled with potash-ley, wood-spirit passes over, and there remains acetate of potash, together with a small quantity of resin and oil, proceeding chiefly from the decomposition of the wood-spirit by the potash. (Weidmann & Schweizer.)

¶ According to Völckel, also, the products obtained by treating lignone or xylite with excess of potash are xylitic naphtha, xylite-oil, and xylite-naphtha, the last chiefly when the air has access. To xylitic naphtha he assigns the formula $C^{12}H^{11}O^3$, and to the oil $C^{12}H^9O$; he supposes both to be formed from lignone by abstraction of water:

$$C^{12}H^{12}O^4 = C^{12}H^{11}O^3 + HO = C^{12}H^9O + 3HO. \text{ ¶}$$

Potassium thrown upon lignone becomes so strongly heated, that the liquid, if not cooled, may take fire. At first, acetylite of potash separates out, without any evolution of gas; afterwards the liquid turns brown, and is ultimately converted into a thick black-brown mass, from which water separates a dark brown oily mixture of mesite, xylitic naphtha, xylite-oil, and xylite-resin, and dissolves a large quantity of acetate of potash, a very small quantity of xylite resin, a very small quantity of an acid body [which precipitates lead and silver salts], and probably also wood-spirit. The potassium first takes oxygen from a portion of the lignone, whereby mesite and potash are produced; the potash thus formed decomposes another portion of the lignone, yielding hypoacetylite of potash and methylic ether; and the latter, finding no water with which to form methylic alcohol, combines with another portion of the potash, forming methylate of potash:

$$5C^6H^6O^{2\frac{1}{2}} + 2K = KO,C^4H^3O^{1\frac{1}{2}} + C^2H^3KO^2 + 4C^6H^6O^2.$$

By the further action of the potassium, the mesite is reduced to xylitic naphtha, then to xylite-oil, and finally to xylite-resin. On the addition of water, the methylate of potash dissolves in the form of aqueous potash and wood-spirit. (Weidmann & Schweizer.) — Respecting the action of potassium on lignone, *compare* Löwig. (*Pogg.* 42, 404.)

Combinations. Lignone mixes in all proportions with *Water*.

It dissolves small quantities of *Phosphorus* and *Sulphur;* the solutions are colourless and become milky when mixed with water. (Gm.) The phosphorus solution, kept in a closed vessel, does not form any acid containing phosphorus, as the solution of phosphorus in acetone does under similar circumstances. (Zeise.)

Lignone dissolves a large quantity of *Iodine,* forming a dark brown solution.

It does not dissolve *Chloride of Calcium,* but sinks into it, making it hot, and swelling it up to a white mass, which gives off the lignone but slowly and incompletely at 100°. It may be mixed with a solution of chloride of calcium in wood-spirit; but on adding more chloride of calcium and agitating, two layers of liquid are formed, the upper of which contains the greater part of the lignone. (Gm.) According to Liebig (*Chim. org.*) lignone dissolves chloride of calcium in all proportions, forming a kind of syrup.

Lignone mixes in all proportions with *Alcohol* and *Ether;* from the latter mixture water separates the ether, which then rises to the surface. (Gm.)

Lignone mixes in all proportions with oil of turpentine; it dissolves very large quantities of camphor, spermaceti, and cholesterin, and a small quantity of olive-oil. It likewise dissolves colophony and shell-lac. (Gm.)

Addenda to Lignone.

Products of the decomposition of Lignone. Reichenbach's Mesite and Scanlan's Liquid.

Methol. C^4H^3 or $C^{20}H^{14}$?

Formed in the distillation of lignone, mesite, mesitene, xylitic naphtha, xylite-oil or xylite-resin, with oil of vitriol.

One part of lignone is distilled with 1 pt. of oil of vitriol; the upper layer of the distillate containing methol together with sulphurous acid, sulphate of methyl, and mesitene, decanted off, shaken up with water and afterwards with weak potash, and subjected to fractional distillation, the first and last portions, which contain mesitene and sulphate of methyl, being set aside; this fractional distillation several times repeated till the distillate no longer smells of sulphate of methyl; and the distillate then set aside in contact with chloride of calcium, and rectified over burnt lime.

Thin, colourless liquid, lighter than water. Boils at about 175°, without any decomposition. Smells like oil of turpentine and has a burning taste.

			Weidm. & Schweizer.
4 C	24	88·89	88·97
3 H	3	11·11	11·02
C^4H^3	27	100·00	99·99

[The boiling point is more in accordance with the formula $C^{20}H^{14}$.]

Methol may be kept without alteration in vessels containing air. It does not mix with oil of vitriol; but if the two liquids are stirred up together from time to time, the oil of vitriol blackens, sulphurous acid is given off, and the methol disappears altogether after a few days. If water be then added, three strata of liquid are formed: the lowest, which is nearly colourless, contains sulphurous, sulphuric, and sulphometholic acids. If therefore it be saturated with lime, the filtrate evaporated, the dry residue exhausted with alcohol, which leaves gypsum undissolved, and the alcohol evaporated, a white crystalline residue is left, consisting of *sulphometholate of lime*, which, when heated, first gives off methol, then blackens and evolves sulphurous acid; it contains 16·02 per cent. of lime, 38·45C, 4·90H, and 41·52 sulphuric acid, whence its formula is $CaO,SO^3 + C^{12}H^9,SO^3$. — The middle stratum of liquid is black and thick; the upper, yellowish. On distilling these two liquids, which cannot well be separated, with water, methol passes over, and there remains methol-resin, which may be freed from the remaining portion of methol by alcohol, and then purified by dissolving in ether and evaporating the filtrate over the water-bath. *Methol-resin* thus obtained is black, heavier than water, soft, melts at a gentle heat, and dissolves in ether and lignone, but not in wood-spirit or alcohol. It contains 86·00 p.c. C, 9·57H, and 4·43 O, and is therefore $C^{24}H^{16}O$. — When methol is distilled with oil of vitriol, part of it goes over undecomposed; sulphurous acid is likewise evolved, together with a very small quantity of acetic acid, and there remains a carbonaceous mass. (Weidmann & Schweizer, *J. pr. Chem.* 23, 48.)

¶ According to Völckel (*Popp.* 84, 101,) the oily substance obtained by treating xylite (or lignone) with an equal weight of oil of vitriol, washing the product with potash, distilling off the undecomposed lignone in the water-bath, and the residual liquid (the so-called methol) over the open fire, is a mixed oxygenated substance, whose boiling-point varies from 100° to 220°. By repeatedly agitating this liquid with strong sulphuric acid, a product was obtained, which after being washed with water, rectified with water, and dehydrated with chloride of calcium, formed a clear, colourless, inflammable liquid, having a peculiar odour, lighter than water, insoluble in water, but soluble in alcohol and ether. Its boiling point was variable, rising from 160° to 220°; the specific gravity of the portion which passed over between 160° and 190° was 0·868; that of the remainder, from 190° to 220°, was 0·879; the composition of both portions corresponded to the formula C^2H^2.

			from 160° to 190°.		from 190° to 220°.
3 C	18	90·00	89·66		89·74
2 H	2	10·00	10·33		10·27
C^2H^2	20	100·00	99·99		100·01

The composition of this liquid is the same as that of the hydrocarbons separated by sulphuric acid from the volatile oils of wood-spirit. ¶

Xylite-oil. $C^{12}H^9O$.

Produced by the action of oil of vitriol, hydrate of potash, or potassium on lignone, mesite, or xylitic naphtha, and by that of oil of vitriol or hydrate of potash on mesitene. Its formation from lignone, mesite, or mesitene is always preceded by that of xylitic naphtha. — The same oil is produced in the decomposition of acetone by potassium, hydrate of potash, or quick lime (p. 15).

Hydrate of potash in large excess is left to act for some time on lignone; water then added; the oily mixture of xylite-oil and xylite-resin which separates, distilled with water, the resin then remaining behind; and the xylite oil which has passed over, several times rectified alone, the portion collected below 200°, which may contain xylitic naphtha, being each time set aside.

Colourless oil, lighter than water; boils above 200°, and passes over undecomposed. Has a peculiar odour, and a bitter burning taste.

		Weidmann & Schweizer. *a.*	*b.*	Löwig. *c.*
12 C	72	80·90	81·38	80·47	80·94
9 H	9	10·11	10·36	10·42	10·27
O	8	8·99	8·26	9·11	8·79
$C^{12}H^9O$	89	100·00	100·00	100·00	100·00

a was obtained from lignone by oil of vitriol, *b* by hydrate of potash, and *c* by potassium.

The oil burns with a bright, sooty flame. — Exposed for some time to the air at temperatures between 50° and 80°, it is wholly converted into brown xylite-resin:

$$2C^{12}H^9O + O = C^{24}H^{18}O^3.$$

It mixes in all proportions with oil of vitriol, evolving sulphurous acid, and forming a dark brown liquid, from which water, added after a while, separates a dark brown oily mixture of xylite-oil and xylite-resin, and dissolves sulphuric and sulphurous acid, together with traces of acetic acid and xylite-resin. Hence it appears that the action of oil of vitriol on this body is almost entirely an oxidizing action. — Xylite-oil distilled with oil of vitriol yields sulphurous acid, acetic acid, and methol, and leaves a carbonaceous mass. — Hydrate of potash makes xylite-oil hot and turns it first brown, then black, and gradually converts it, with formation of acetate of potash and a resin, into a mass having the hardness of stone. — Potassium acts but feebly on it even when heated, and slowly dissolves in the oil without evolution of gas, the oil at the same time becoming brown and viscid. Water then added to it dissolves the acetate of potash previously formed, and separates a brown oily mixture of xylite-oil and a resin having the same composition as that which is formed by the action of hydrate of potash. It contains 82·82 p.c. C, 10·21 H, and 6·97 O; hence its formula is $C^{18}H^{26}O^{2}$.

Xylite-oil is nearly insoluble in water, but dissolves readily in wood-spirit, ether, alcohol, and lignone. (Weidmann & Schweizer, *J. pr. Chem.* 23, 42.)

Brown Xylite-resin. $C^{24}H^{18}O^{3}$.

Formed by the action of oil of vitriol, hydrate of potash, or potassium on lignone, mesite or xylitic naphtha, and of oil of vitriol or hydrate of potash upon mesitene, its formation being always preceded by that of xylitic naphtha. This resin is also formed when xylite-oil is oxidized, either by oil of vitriol or by exposure to the air; also in the decomposition of acetone by potassium or hydrate of potash (p. 15).

Hydrate of potash is allowed to act in excess on anhydrous lignone, till the mixture becomes brown, whereupon water is added to it. (If the action be suffered to go on too long, the xylite-oil produced at the same time is converted by the potash into another resin (*vid. sup.*) which is difficult to separate from brown xylite-resin.) The oily mixture separated by the addition of water is distilled, with frequent renewal of the water, as long as xylite-oil passes over with the distillate; the residue is then dissolved in alcohol; the solution evaporated in the water-bath; and the fused residue left there for some time longer.

Red-brown; heavier than water; brittle at temperatures below 150°; soft and tenacious between 15° and 20°; melts below 100°. Its aqueous solution has an acid reaction.

			Weidmann & Schweizer.	
			Brown Xylite-resin.	*Yellow Xylite-resin.*
24 C	144	77·42	78·85	80·12
18 H	18	9·68	9·53	10·04
3 O	24	12·90	11·62	9·84
$C^{24}H^{18}O^{3}$	186	100·00	100·00	100·00

Dissolves in oil of vitriol in nearly all proportions, causing rise of temperature and evolution of sulphurous acid, and forming a black greasy mass. If this mass be treated with water after some time, the water separates a resinous mixture and takes up sulphuric and sulphurous acids, together with traces of acetic acid and a resin; from the resinous mixture,

alcohol of 70 per cent dissolves out unaltered brown xylite-resin, leaving a brown pulverulent resin which does not soften at 100°, but fuses at a stronger heat into a black mass. It contains 83·27 p.c. C, 9·38 H, and 7·35 O; hence its formula is $C^{18}H^{32}O^3$. — Brown xylite-resin distilled with oil of vitriol yields sulphurous acid, acetic acid, a small quantity of methol, and a black residue.

Brown xylite-resin does not dissolve in water and potash-ley, but readily in alcohol, ether, and lignone; the alcoholic solution does not precipitate neutral acetate of lead. (Weidmann & Schweizer, *J. pr. Chem.* 23, 45.)

Yellow Xylite-resin.

Produced by the action of oil of vitriol upon lignone, mesite, and xylitic naphtha, probably by a catalytic action on the isomeric brown xylite-resin first produced.

The oil which separates on adding water after the decomposition of lignone by oil of vitriol, is distilled with water; the residual mixture of yellow and brown xylite-resin dissolved in strong alcohol; the solution mixed with alcohol of 70 per cent, which precipitates the yellow resin; and the precipitate freed from the brown resin thrown down at the same time, by repeated washing with strong alcohol and precipitation with weak alcohol. It is then melted for some time on the water-bath [sic ?].

The resin is reddish yellow, brittle, and does not become soft by friction like the brown resin. Its melting point is much above 100° [sic ?].

For the analysis, which perhaps shows it to be isomeric with the brown resin, *vid.* p. 49.

Yellow xylite-resin behaves with oil of vitriol like the brown resin. It does not dissolve in water or potash-ley. It is nearly insoluble in weak spirit, but dissolves in strong alcohol and in ether, forming a yellow solution. Its alcoholic solution does not precipitate an alcoholic solution of acetate of lead; ammonia added to the solution throws down yellow flakes. (Weidmann & Schweizer, *J. pr. Chem.* 23, 47.)

Xylitic Naphtha. $C^6H^6O^{14} = C^{12}H^{12}O^3$.

Produced by the action of oil of vitriol, potash, or potassium on lignone, mesite, or mesitene.

A small quantity of hydrate of potash is placed for some time in contact with lignone; water added; the oily mixture of xylitic naphtha, mesite, xylite-oil and xylite-resin separated from the watery solution; the distillate rectified alone, whereupon the xylitic naphtha passes over chiefly between 100° and 120°; and this product rectified several times to free it from the remaining portion of mesite and xylite-oil, the portion which passes over between 100° and 120° being always collected apart till it exhibits a tolerably constant boiling point of 110°.

Colourless, mobile liquid, lighter than water, boiling at 110°, and capable of being distilled without decomposition. Smells like oil of peppermint, and has a burning taste.

			Weidm. & Schw.	Löwig.
6 C	36	66·67	66·82	66·64
6 H	6	11·11	11·08	10·23
1½ O	12	22·22	22·10	23·13
	54	100·00	100·00	100·00

The naphtha analyzed by Löwig was obtained by treating lignone with potassium. — Xylitic naphtha is regarded as methylic ether + oxide of acetyl = $C^2H^3O + C^4H^3O^{1\frac{1}{2}}$. — Völckel assigns to xylitic naphtha the formula $C^{12}H^{11}O^3$, and supposes it to be formed from xylite by abstraction of water.

This liquid burns with a smoky flame. Mixed with oil of vitriol, it turns brown and thickens; water then separates from it an oil consisting of xylitic naphtha, xylite-oil, and yellow and brown xylite-resin. The aqueous solution contains acetic acid, sulphomethylic acid, and a trace of resin. — When xylitic naphtha is distilled with oil of vitriol, sulphurous acid, acetic acid, mesitene, and methol distil over, leaving a carbonaceous residue. — Hydrate of potash in excess forms with xylitic naphtha a black-brown mass from which water separates a viscid mixture of xylite-resin and xylite-oil, and takes up acetic acid, together with a small quantity of wood-spirit. — Potassium acts violently on xylitic naphtha, but without evolution of gas, forming a black-brown viscid mixture containing the same products as that which is obtained by the action of hydrate of potash. [For the complicated equations given for these reactions, vid. *J. pr. Chem.* 23, 37 to 39].

Xylitic naphtha dissolves very sparingly in water, but readily in alcohol, ether, and lignone. (Weidmann & Schweizer, *J. pr. Chem.* 23, 35.)

Weidmann & Schweizer's Mesite. $C^6H^6O^2 = C^{12}H^{12}O^4$.

This mesite differs from Reichenbach's. It occurs, in small quantity only, in wood-vinegar; it is formed by the action of oil of vitriol, potash, or potassium on lignone, and by the action of oil of vitriol or potash upon mesitene.

Preparation. 1. After lignone has been separated from wood-spirit by distillation over chloride of calcium (VII, 259), there still remains with it a certain portion of mesite, which, by reason of its small quantity, cannot be separated by water. The greater part of the lignone is therefore distilled from this mixture, till the liquid which passes over becomes turbid on the addition of water; the residue in the retort, consisting chiefly of mesite, freed from lignone by repeated agitation with water; then distilled over the water-bath, with change of receiver, because the portion which first passes over may still contain lignone; and the pure mesite which passes over towards the end of the process, finally dehydrated by distillation over chloride of calcium.

2. Lignone is placed in contact with hydrate of potash (not in too great quantity) till it begins to turn brown; mixed after a while with water; the oily liquid which separates, distilled, xylite-resin then remaining behind; the distillate, consisting of mesite, xylitic naphtha, and xylite-oil, rectified; and the mesite, which passes over till the temperature rises to 80°, collected apart, and purified by several distillations, the last portions of distillate being always set aside.

Properties. Colourless, mobile liquid, lighter than water. Boils somewhat above 70°. Vapour-density 2·833 to 2·852 [which does not agree with the assumed formula]. Has a pleasant ethereal odour and a burning taste.

			Weidmann & Schweizer. (1)	(2)
6 C	36	62·07	62·31	62·26
6 H	6	10·34	10·57	10·65
2 O	16	27·59	27·12	27·09
$C^6H^6O^2$	58	100·00	100·00	100·00

¶ Völckel also finds that mesite is isomeric with acetone and xylite. The less volatile portions of the liquid obtained by treating crude wood-spirit with chloride of calcium (p. 43), he finds to contain decomposition-products formed from xylite by abstraction of water. ¶

Mesite burns with a bright but sooty flame. — It mixes with oil of vitriol, producing great evolution of heat. Water added after a while to the dark brown mixture, takes up sulphomethylic and acetic acid, and leaves a thick brown oil, consisting of undecomposed mesite, xylitic naphtha, xylite-oil, and brown and yellow xylite-resin. Mesite distilled with oil of vitriol continually gives off sulphurous acid, and like lignone, yields first mesitene, then methol and acetic acid, and leaves a carbonaceous residue. — Hydrate of potash, in contact with mesite, immediately separates a potash-salt, which yields acetic acid when distilled with sulphuric acid; soon, however, it undergoes further decomposition, and yields xylitic naphtha, xylite-oil, and xylite-resin. [The equations should be looked to.]

Mesite requires 3 pts. of water to dissolve it. (Weidmann & Schweizer, *J. pr. Chem.* 23, 29.)

Mesitene. $C^6H^8O^3=C^{12}H^{12}O^6$.

Produced by distilling lignone, mesite, or xylitic naphtha with oil of vitriol. Dry lignone thus treated yields but a small quantity of mesitene, because the greater part of it is soon converted into sulphomethylic acid, and thereby escapes oxidation; but hydrated lignone, which is not so readily converted into sulphomethylic acid, yields a large quantity of mesitene.

Equal parts of lignone and oil of vitriol are distilled with a small quantity of water, and the receiver changed as soon as the distillate begins to separate into two layers, because from that time, the quantity of mesitene which passes over is but small, its place being taken by methol and acetic acid. The first distillate, which consists of mesitene and admixed lignone, is shaken up with chloride of calcium, which dissolves in the lignone; the mesitene which floats on the surface, taken off; freed from the remaining portion of lignone by repeated agitation with a small quantity of water; and distilled, first over chloride of calcium and then over quick lime, the last portion of the distillate, which may contain methol, being each time set aside.

Colourless, mobile liquid, of sp. gr. 0·805; boils constantly at 63°. Vapour-density 2·873. Has a pleasant, ethereal odour.

			W. & S.
8 C	36	54·55	54·87
6 H	6	9·09	9·14
3 O	24	36·36	35·99
$C^6H^6O^3$	66	100·00	100·00

This compound may be regarded as acetylite [=aldehydate] of methyl = $C^2H^3O,C^4K^3O^2$. — [According to the formula $C^8H^8O^4$, the calculated vapour-density would be 3·0505; but according to the formula $C^6H^6O^3$, the calculated density differs still more widely from that found by experiment, requiring therefore the hypothesis of an unusual mode of condensation]. — ¶. According to Völckel (*Ann. Pharm.* 80, 311) Weidmann & Schweizer's mesitene is a mixture of pure xylite (p. 43) with acetate of methyl. ¶

Mesitene burns with a bright but smoky flame. Mixed with oil of vitriol, it becomes strongly heated and assumes a brown colour, light at first, but becoming gradually darker. Water added to the mixture after some time separates an oil consisting of mesitene, xylitic naphtha, xylite-oil, and xylite-resin, and takes up acetic and sulphomethylic acid. — Mesitene distilled with an equal quantity of oil of vitriol, passes over undecomposed at first, and then yields sulphurous acid, acetic acid, and methol. — When it is distilled with excess of oil of vitriol, only a small quantity of methol is obtained, the product consisting almost wholly of sulphurous and acetic acid. — Distilled with oil of vitriol and acid oxalate of potash, it does not yield oxalate of methyl. — Hydrate of potash in excess forms with mesitene a gelatinous mass which gradually turns brown. Water, added after some time, takes up, besides free potash, a large quantity of a potash-salt which yields acetic acid by distillation with sulphuric acid, and is therefore acetylite of potash, whilst a mixture of mesite, xylitic naphtha, xylite-oil, and xylite-resin remains behind. — Potassium in contact with mesitene produces great heat but no evolution of gas, and immediately separates a white salt, which yields acetic acid by distillation with sulphuric acid, and must be regarded as acetylite of potash ($KO,C^4H^3O^{11}$); it dissolves on addition of water, a colourless oily mixture of mesitene and xylitic naphtha separating at the same time. [The equations for these decompositions should be looked to.]

Mesitene dissolves in 3 parts of water (Weidmann & Schweizer, *J. pr. Chem.* 23, 30).

Reichenbach's Mesite.

Produced in all dry distillations, and therefore occurs in beech, coal, and animal tar. (But the empyreumatic oil obtained from hemp-oil does not contain anything soluble in water which behaves like mesite. Hess, *Pogg.* 38, 384.)

Preparation. 600 kilogrammes of beech-tar are distilled at a very gentle heat, till only the most volatile portion has passed over; this portion consists of about 20 litres of light, pale yellow oil and a watery liquid, which, at certain stages of the distillation mix together again through the medium of the mesite. The whole distillate is neutralized with carbonate of potash and rectified over the oil-bath, as long as oil continues to pass over; and the pale yellow oil is freed from the small

quantity of watery liquid which has passed over with it, and distilled in the water-bath over a large quantity of slaked lime, which retains creosote, picamar, and a yellow colouring principle. If this distillate becomes gradually yellow by exposure to the air, it must be once more distilled over lime, after which it will remain unaltered. Lastly, to separate the eupione, the distillate is briskly agitated with 15 times its bulk of water; the aqueous solution of the mesite separated from the undissolved eupione, which floats on the top; the former distilled in a gently heated water-bath, the distillation being stopped as soon as the water in the both begins to boil; and the mesite which has passed over, purified from water and wood-spirit by repeated distillation over chloride of calcium.

Transparent, colourless, very mobile liquid, of sp. gr. 0·805; boils at 62°; has a pleasant aromatic and spirituous odour, and a slightly burning taste.

Mesite burns with a clear whitish yellow flame somewhat bluish below, and without smoke. — It absorbs chlorine gas with moderate rise of temperature, acquiring after a while, a very powerful odour which excites tears. It dissolves bromine, with heat and decoloration. Mixed with strong nitric acid, it intumesces strongly after a while; and with oil of vitriol it becomes heated to sudden ebullition, but without yielding an ether; water then added to the mixture separates oils having the odour of coffee and of strawberries.

Mesite is sometimes in a condition to take up $\frac{1}{2}$ pt. of water, sometimes to dissolve in 2 pts. of water. The solution of phosphorus in mesite does not shine in the air. Mesite dissolves sulphur and large quantities of iodine. It mixes in all proportions with sulphide of carbon. Dissolves boracic acid when heated. Mixes with dilute ammonia and potash, but not with strong potash, and is not decomposed thereby. Dissolves uranic nitrate and chloroaurate of sodium, but not chloride of calcium. Mixes in all proportions with ether, alcohol, volatile and fixed oils, and dissolves many camphors, fats, resins and organic acids (Reichenbach, *Schw.* 69, 176; *abstr. Ann. Pharm.* 10, 298).

According to Berzelius, Reichenbach's mesite is acetate of methyl; in that case, there must be a lighter liquid mixed with it; for the sp. gr. of acetate of methyl is 0·909; that of Reichenbach's mesite 0 805 — Compare also Liebig (*Ann. Pharm.* 10, 315).

Scanlan's Liquid.

Crude wood-vinegar is distilled till 15 per cent has passed over; the residue neutralized with lime; the pitch which is thereby separated, taken off; the liquid distilled as long as the distillate continues to be lighter than water; and this distillate repeatedly rectified. A strongly coloured liquid of sp. gr. 0·9 then passes over first, afterwards a liquid of sp. gr. 0·83, then water and an empyreumatic oil which blackens by keeping. The first and most volatile liquid, of sp. gr. 0·9, is collected apart, decolorized by animal charcoal, and rectified over the water-bath.

The liquid thus obtained is colourless; has a density of 0·911; boils at 55·6°; has a strong and repulsive odour; reddens litmus only when *exposed to the air; is highly* combustible; is immediately decomposed by *potash or lime, with formation* of an acetate of the alkali; and mixes

with water in all proportions, the combination being attended with rise of temperature and condensation (Scanlan, *Phil. Mag. J.* 7. 395; also *J. pr. Chem.* 7. 97).

¶ *Volatile Oils, produced by the distillation of Wood.*

These oils form the first portion of the liquid which passes over in the distillation of wood-tar; they are lighter than water. The crude oil is yellowish, and turns brown by keeping. It was distilled first with water and then alone. In the latter distillation, the boiling point rose from 75° to 205°. By treating the distillates with alcoholic potash-solution or distilling them over solid caustic potash, then washing, drying, and again subjecting them to fractional distillation, a large number of colourless liquids were obtained, of different but not constant boiling points; these liquids were mixtures which could not be separated into their component parts. — The portion which distilled over between 105° and 110° had a density of 0·841 and contained about 78·2 p.c. carbon and 8·9 hydrogen; that which passed over between 190° and 205° had a density of 0·877, and contained 85·9 p.c. carbon and 9·7 hydrogen: the properties and composition of the other liquids lay between these limits. In general the atomic proportion of the carbon and hydrogen was the same in them all, viz. 3C to 2H, the amount of oxygen decreased as the boiling point rose. The oils which distilled over between 160° and 205° were much less powerfully attacked by sulphuric and nitric acid than those which boiled at lower temperatures. — When the oils having the higher boiling points were agitated with sulphuric acid, there remained an oily liquid, which, after being washed and distilled with water, was colourless and mobile. Its boiling point rose from 155° to 205°; the densities of the various portions which passed over at different temperatures between these limits ranged from 0·864 to 0·881; but in composition they were nearly identical, the proportion of carbon varying only from 89·60 to 89·99, and that of hydrogen from 9·99 to 10·25, numbers which accord very nearly with the formula C^3H^2. — From these facts, Völckel infers that the light oils obtained in the distillation of wood, are all either hydrocarbons having the composition C^3H^2, or compounds of these hydrocarbons with oxygen. Of the same composition is likewise the less volatile portion of the empyreumatic oil which separates out on saturating wood-vinegar with lime — that portion, namely, which boils above 100°. — Oils of the same composition are also obtained by distilling lignone with oil of vitriol, pp. 44, 45: (Völckel, *Pogg.* 82, 496; abstr. *Ann. Pharm.* 80, 306; *Jahresber.* 1851, 524).

Volatile Oils obtained from crude Wood-spirit. When crude wood-spirit is mixed with water, a pale yellow oily liquid rises to the surface. The boiling point of this liquid rises gradually from 90° to 200°, and it does not appear to be separable into its component parts by fractional distillation. When shaken up with oil of vitriol, it yields a brown-red viscid mass, above which floats a transparent, aromatic liquid. This liquid, after being washed with alkaline water, dried over fused chloride of calcium, and distilled over anhydrous phosphoric acid, still exhibits a boiling point varying from 108° to 170°; the largest portions however, consisting of hydrocarbons, pass over between certain small ranges of temperature, viz. from 108° to 112°; from 128° to 130°; from 145° to 148°; and from 164° to 168°. — The portion which distils over between

108 and 112° consists of *toluol* $C^{14}H^8$; from 128° to 130°, of *xylol*, $C^{16}H^{10}$; and from 145° to 148°, of *cumol*, $C^{18}H^{12}$, which is isomeric with mesitilol. The portion of the distillate obtained between 164° and 168° has the same composition and vapour-density as cumol or mesitilol, but is not identical with either. Some samples of commercial wood-spirit also yield a more volatile oily liquid, which boils from 58° to 100°, and is chiefly a mixture of methylic acetate with Fremy's metacetone, $C^{12}H^{10}O^2$ (Cahours, *Compt. rend.* 30, 319, *Chem. Soc. Qu. J.* 3, 183; *Jahresber.* 1850, 491). ¶

Conjugated Compounds containing Ammonia.

¶ **Ethylamine.** $C^4H^7N = C^4H^4,H^3N = \left.\begin{matrix} H \\ H \\ C^4H^5 \end{matrix}\right\}N.$

WURTZ. *Compt. rend.* 28, 223 and 323; *Ann. Pharm.* 71, 930; *Chem. Soc. Qu. J.* 3, 90. — More fully: *N. Ann. Chim. Phys.* 30, 443. (*Vid.* also authorities cited VII, 313.)

Ethylamide, Ethyl-ammonia, Ethylia, Ethamine, Ethyliaque, Aethyliak. — Found in the *oleum animale Dippelii.* (Anderson.)

Formation. 1. By the action of potash on cyanate or cyanurate of ethyl (Wurtz):

$$C^2NO,C^4H^5O + 2(KO,HO) = 2(KO,CO^2) + C^4H^7N.$$

2. By the action of potash on ethyl-urea (Wurtz):

$$C^6H^8N^2O^2 + 2(KO,HO) = 2(KO,CO^2) + NH^3 + C^4H^7N.$$

3. By the action of bromide or iodide of ethyl on ammonia (Wurtz, Hofmann):

$$NH^3 + C^4H^5Br = C^4H^7N,HBr.$$

4. By the action of chloride or iodide of ammonium on alcohol or ether. When sal-ammoniac is heated with absolute alcohol in sealed tubes, ether is formed, its production beginning at 260°; and at 400°, when the decomposition of the alcohol is nearly complete, the liquid separates into an ethereal and a watery stratum, the latter containing the hydrochlorates of certain ethyl-bases, the most abundant of which is ethylamine:

$$C^4H^6O + NH^3,HCl = C^4H^7N,HCl + HO.$$

Iodide of ammonium acts in a similar manner (Berthelot, *N. Ann. Chim. Phys.* 38, 63). — 5. By the decomposition of sulphethamic acid $C^{16}H^{23}NO^4,4SO^3$, under the influence of acids or alkalis, whereby that compound is resolved into ethylamine, sulphuric acid, and probably also alcohol and isethionic acid (Strecker, *Ann. Pharm.* 75, 50):

$$C^{16}H^{23}NO^4,4SO^3 + 4HO = C^4H^7N + 2(HO,SO^3) + 2C^4H^6O^2 + C^4H^6O^2,2SO^3.$$

6. Sulphide of aldehyde-ammonia heated with lime is resolved into sulphuric acid and ethylamine (Gössmann, *Ann. Pharm.* 91, 122):

$$C^4H^4O^2,NH^3,2SO^2 = 2SO^3 + C^4H^7N.$$

Preparation. 1. By decomposing cyanic ether with potash. The action takes place at ordinary temperatures and is attended with great

evolution of heat; hence it is best to mix the liquids in a bottle having a well ground stopper, which must be tightly secured, and to cool the bottle externally. The decomposition is complete in about five minutes, the vessel then containing nothing but ethylamine and carbonate of potash. The liquid is then distilled, and the vapour of ethylamine passed into a receiver containing a little water and cooled externally. To obtain the anhydrous base, the aqueous solution thus formed is saturated with hydrochloric acid; and the hydrochlorate of ethylamine crystallized by evaporation, thoroughly dried, and gently heated with twice its weight of quick lime in a long glass tube, closed at one end, the mixture occupying the lower half of the tube, while the upper half is filled with fragments of caustic potash to dry the vapour of ethylamine as it is evolved. The dry vapour then passes through a delivery-tube into a small flask or U-tube surrounded with a freezing mixture, and is there condensed to a liquid. (Wurtz.) — 2. By the action of ammonia on bromide or iodide of ethyl. — *a*. Strong ammonia is enclosed together with excess of bromide of ethyl in a combustion-tube two teet long, and the sealed tube immersed in boiling water. Decomposition takes place quickly, with ebullition, and is complete in about a quarter of an hour, its completion being indicated by the volume of the bromide of ethyl remaining constant instead of diminishing. The tube then contains hydrobromate of ethylamine, from which the base may be obtained by distillation with potash or lime. (Hofmann, *Chem. Soc. Qu. J.* 3; 300.) — *b*. Iodide (or bromide) of ethyl is mixed with an equal volume of absolute alcohol, the mixture kept in a state of gentle ebullition in a tubulated retort the neck of which is directed upwards and well cooled, and dry ammoniacal gas passed into it for a considerable time. After cooling it is again treated with ammoniacal gas and then left to stand for some days, to complete the conversion of the iodide of ethyl into hydriodate of ethylamine, the completion of the change being known by the liquid no longer becoming turbid when mixed with water. The solution is evaporated to dryness over the water-bath, and the saline mass gently heated with strong solution of potash in a small flask or retort. Vapour of ethylamine is then evolved and may be either passed into water, or dried by passing it over hydrate of potash and condensed in a tube surrounded with ice and salt. (Wöhler, *Ann. Pharm.* 86, 374.) — 3. By decomposing sulphethamic acid with potash. Vapour of anhydrous sulphuric acid is passed into ether, the product (crude sulphuric ether, VIII, 413,) freed from ether by agitation with water, and a stream of ammoniacal gas passed through it. The resulting sulphethamate of ammonia is boiled with carbonate of lead or baryta till all the ammonia is expelled; potash, then added; and the ethylamine which is set free by the decomposition of the sulphethamic acid, distilled off as above. (Strecker.) — 4. By distilling sulphite of aldehyde-ammonia with lime (Gössmann : for details, vid. *Ann. Pharm.* 91, 122).

Properties. Anhydrous ethylamine is a transparent, colourless, very mobile liquid, of specific gravity 0·6964 at 8°. Does not solidify at the temperature of a mixture of solid carbonic acid and ether. Boils at 18·7°. (Wurtz.) Vapour density at 43° and under a pressure of 773·04 mm.= 1·5767. (Izarn.) Has a very pungent ammoniacal odour, a strong alkaline reaction, and is highly caustic, a small drop of the concentrated aqueous solution placed upon the tongue producing a burning pain and acute inflammation. Forms very dense white fumes with hydrochloric acid

gas, and makes a hissing noise when strong hydrochloric acid is dropt into it. (Wurtz.)

			Wurtz.			Vol.	Density.
4 C	24	53·33	53·61	C-vapour	4		1·6640
7 H	7	15·55	15·60	H-gas	7		0·4851
N	14	31·12	31·45	N-gas	1		0·9706
C^4H^7N	45	100·00	100·66		2		3·1197
					1		1·5598

May be regarded: (1) as C^4H^5N,H^2, *i. e.* as a compound of 2H with a nucleus C^4H^6, in which 1H is replaced by N;—(2), as C^4H^6Ad, *i. e.* as the same nucleus in which 1H is replaced by Ad;—(3), as C^4H^3Ad,H^2, *i. e.* as a compound of 2H with ethylene, C^4H^4, in which 1H is replaced by Ad;—(4), as C^4H^4,NH^3, *i. e.* as ammonia coupled with ethylene; or lastly, as $\left.\begin{matrix}H\\H\\C^4H^5\end{matrix}\right\}N$, *i. e.* as ammonia in which 1H is replaced by ethyl.

(Compare VII, 16, 17 and 186).

Decompositions. 1. Ethylamine vapour passed through a red hot porcelain tube is resolved into ammonia, hydrocyanic acid, hydrogen, and a small quantity of a compound of hydrogen and carbon. — 2. On the approach of a burning body, it takes fire and burns with a yellowish flame. — 3. *Iodine* decomposes the aqueous solution of ethylamine, forming hydriodate of ethylamine, and a substitution product, *biniodethylamine*, which cannot be distilled without decomposition:

$$2C^4H^7N + 4I = HI + C^4H^7N,HI + C^4(H^5I^2)N.$$

Bromine and *Chlorine* produce similar reactions. (Wurtz.) — 4. When a crystal of *nitrate of potash* is introduced into a solution of hydrochlorate of ethylamine acidulated with hydrochloric acid, *nitrous* ether is evolved in considerable quantity, and if set on fire at the mouth of the tube, burns with a flame coloured light-green at the edges:

$$C^4H^7N + 2NO^3 = C^4H^5O,NO^3 + 2HO + 2N.$$

At the same time, a small quantity of yellow aromatic oil is produced, having a sweet, biting taste, and a high boiling point. (Hofmann, *Chem. Soc. Qu. J.* 3, 131.) — 3. *Oil of mustard* forms with ethylamine an oily base called *Thiosinethylamine*, having the composition $C^{12}H^{12}N^2S^2$. (Hinterberger, *Ann. Pharm.* 83, 346.)

Combinations. 1. Ethylamine mixes with *Water* in all proportions, the act of mixing being attended with evolution of heat. The solution has a certain degree of viscidity which distinguishes it from aqueous ammonia; the whole of the ethylamine may be expelled by continued boiling.

2. Ethylamine has a powerful affinity for *Acids*, neutralizing them as completely as ammonia: it expels ammonia from ammoniacal salts. When a mixture of ethylamine and ammonia is mixed with half the quantity of sulphuric acid required to neutralize it and distilled, ammonia is given off, and the residue consists of sulphate of ethylamine containing mere traces of ammonia. — Ethylamine precipitates metallic salts nearly in the same manner as methylamine (VII, 315); hydrated oxide of copper is however less soluble in ethylamine than in methylamine. With

salts of alumina it forms a white gelatinous precipitate which dissolves in excess of ethylamine as easily as in potash. (Wurtz.)

The ethylamine-salts may be supposed to contain a metalloïdal radical *ethylium* C^4H^5N, analogous to ammonium: thus *hydrochlorate of ethylamine* $=C^{12}H^7N,HCl=C^{12}H^5N,Cl=$*chloride of ethylium*.

Carbonate of Ethylamine. — *a. Anhydrous.* Anhydrous ethylamine absorbs dry carbonic acid gas, forming a snow-white pulverulent mass, soluble in water. The solution does not precipitate chloride of barium immediately, but only after a while, and with the aid of heat. (Wurtz.)

			Wurtz.
5 C	30	44·77	44·37
7 H	7	10·44	10·65
N	14	20·89	
2 O	16	23·90	
C^4H^7N,CO^2	67	100·00	

Analogous to anhydrous carbonate of methylamine (VII, 316), and to Rose's *carbonate of ammon* (II, 430).

b. Hydrated. A mixture of hydrochlorate of ethylamine and carbonate of soda, both thoroughly dry, distilled in a small retort, gave off white vapours, which condensed to a white powder; afterwards, thin streams of liquid ran down the neck of the retort, and solidified in the receiver to a crystalline mass saturated with a very thick liquid. The crystals were rapidly pressed between folds of paper to free them from the liquid, but did not yield definite results when analyzed. — This salt is strongly alkaline, has an ammoniacal odour, and even at ordinary temperatures gives off vapours which turn red litmus paper blue. Very deliquescent. Dissolves the hydrated carbonates of zinc and copper. (Wurtz.)

Sulphate of Ethylamine. Deliquescent; uncrystallizable; very soluble in alcohol; dries up in vacuo to a transparent gummy mass. (Wurtz.)

Hydrosulphate of Ethylamine. Obtained in colourless crystals by passing dry sulphuretted hydrogen gas into a flask containing anhydrous ethylamine, surrounded with ice and previously filled with hydrogen. — Very fusible and volatile. The melted salt solidifies on cooling, in beautiful crystals, the form of which appears to be a rhombic prism with rectangular base and terminated by four-sided summits. The vapour is inflammable. The salt, when exposed to the air, turns yellow, absorbs moisture, and liquefies in yellow drops. Its solution dissolves hydrated sulphide of antimony, forming a colourless liquid, which when evaporated deposits an orange-coloured powder. (Wurtz.)

Hydriodate of Ethylamine. Formed: 1. By the direct combination of ethylamine and hydriodic acid. (Wurtz.) — 2. By the action of iodine on aqueous ethylamine (Wurtz, p. 58). — 3. By the action of iodide of ammonium on alcohol or ether (Berthelot, p. 56). — 4. By the action of ammonia on iodide of ethyl (Wöhler). — For the preparation by the last method, see page 57. — Crystalline. Gives off ethylamine when distilled with lime or potash.

Hydrobromate of Ethylamine. Similar to the hydriodate.

Hydrochlorate of Ethylamine or *Chloride of Ethylium.* — Formation similar to that of the hydriodate. — Prepared by saturating with hydrochloric acid the aqueous solution of ethylamine, which is obtained by distilling cyanic acid with potash (p. 54). On evaporating to dryness, dissolving the residue in strong boiling alcohol, and cooling the solution, the salt is deposited in large crystalline laminæ. From the aqueous solution it crystallizes in striated prisms. Fuses between 76° and 80°, and solidifies on cooling in a semitransparent, crystalline mass. Gives off vapours at a higher temperature; boils between 315° and 320°; and if then left to cool, solidifies in a milk-white, amorphous mass, whose melting point is above 260°. The crystals are very deliquescent. On treating the aqueous solution with amalgam of potassium, hydrogen is given off and a solution of ethylamine formed. (Wurtz.)

			Wurtz.
4 C	24·0	29·44	28·93 — 29·52
8 H	8·0	9·81	9·94 — 9·99
Cl	35·4	43·55	43·58
N	14·0	17·20	
C^4H^7N,HCl or C^4H^5N,Cl	81·4	100·00	

Nitrate of Ethylamine. — Obtained by saturating ethylamine with nitric acid. — Very deliquescent; crystallizes from the aqueous solution in thin laminæ. The syrupy mother-liquor, when heated, gives off gases which burn with a yellow flame, and yields a brown watery distillate with a few drops of oil floating on the surface; the residue is a brown mass which ultimately becomes charred. (Wurtz.)

Chloromercurate of Ethylamine. Obtained by mixing the aqueous solutions of corrosive sublimate and hydrochlorate of ethylamine in equivalent quantities. Crystallizes more readily than the corresponding salt of methylamine, but forms smaller crystals. From the alcoholic solution it is deposited in small white scales.

			Wurtz.
4 C	24·0	11·07	11·01
8 H	8·0	3·68	3·88
2 Cl	70·8	32·66	32·71
Hg	100·0	46·13	
N	14·0	6·46	
$C^4H^7N,HCl + HgCl$ or $C^4H^5NCl + HgCl$	216·8	100·00	

Chloro-aurate. — Prepared like the preceding salt. — Forms very fine, golden yellow, prismatic crystals, soluble in water, alcohol, and ether. (Wurtz.)

			Wurtz.
4 C	24·0	6·21	6·21
8 H	8·0	2·07	2·38
4 Cl	141·6	36·63	36·83
Au	199·0	51·47	51·39
N	14·0	3·62	
$C^4H^7N,HCl + AuCl^3$ or $C^4H^5NCl,AuCl^3$	386·6	100·00	

Chloroplatinate. Prepared by mixing the concentrated solutions of bichloride of platinum and chloride of ethylium, adding alcohol, pressing the resulting yellow precipitate, and dissolving it in boiling water. On cooling, the double salt separates in beautiful tablets of a deep orange-yellow colour. (Wurtz.)

				Wurtz.
4 C	24·0	9·58		9·48
8 H	8·0	3·19		3·31
3 Cl	106·2	42·27		42·65
Pt	99·0	39·40		39·08
N	14·0	5·56		
$C^4H^7N,HCl,PtCl^2$ or $C^4H^8NCl,PtCl^2$	251·2	100·00		

Compounds of Ethylamine with Protochloride of Platinum. — *a.* $2(PtCl,C^4H^7N) = 2C^4H^7N,PtCl + PtCl$. — Ethylamine acts readily on protochloride of platinum, causing considerable rise of temperature, and converting it into a chamois-coloured salt, insoluble in water, and agreeing in composition with the above formula. (Wurtz.)

			Wurtz.
8 C	48·0	13·38	13·51
14 H	14·0	3·90	4·02
2 Pt	198·0	55·19	54·75
2 N	28·0	7·80	
2 Cl	70·8	19·73	
$2(PtCl,C^4H^7N)$	358·8	100·00	

Analogous to Magnus's green compound, $2NH^3,PtCl + PtCl$. — It may also be regarded, according to Gerhardt's nomenclature and formulæ, as *Chloroplatinate of Diplatosethylamine*, $PtCl^2H,N^2C^4H^{13}Pt$. (*vid.* VI, 304; VII, 318.)

b. $C^8H^{13}PtN^2,HCl = 2(C^4H^7N),PtCl$. Formed by heating the salt *a* with excess of ethylamine. To prevent loss of ethylamine, it is best to heat the mixture in a small sealed flask, as in the preparation of the corresponding salt of methylamine. (VII, 318.) The chamois-coloured powder dissolves after a while, sometimes completely, sometimes leaving a black detonating residue probably analogous to fulminating platinum. (VIII, 387.) The solution filtered and evaporated deposits splendid colourless prisms, which dissolve pretty readily in water, but sparingly in alcohol. They contain 2 At. water of crystallization.

			Wurtz.
8 C	48·0	19·82	20·05
16 H	16·0	6·61	7·15
Pt	99·0	40·72	40·23
Cl	35·4	14·66	
2 N	28·0	11·56	
2 O	16·0	6·63	
$2(C^4H^7N),PtCl + 2HO$	242·4	100·00	

This compound is analogous to Reiset's first chloride, $2NH^3,PtCl$. (VI, 300.) — According to Gerhardt's notation, it may be regarded as the *Hydrochlorate of Diplatosethylamine*, $N^2C^4H^{13}Pt,HCl$.

Platinosulphate of Ethylamine, $2C^4H^7N,PtSO^4$. The solution of the

preceding compound *b* mixed with sulphate of silver, yields chloride of silver, and a filtrate which, when evaporated, deposits the platinosulphate in colourless crystals of considerable size. The salt is purified by dissolving it in hot water and adding absolute alcohol, which throws it down in the form of a white precipitate. (Wurtz.)

				Wurtz.
8 C	48	20·22		20·12
13 H	13	5·97		6·04
Pt	99	41·67		41·40
2 N	28	11·83		
SHO^4	49	20·31		
$2(C^4H^7N),PtSO^4$	237	100·00		

Wurtz regards Reiset's first base as $NH^3 + NH^2Pt$, assigning to it the name of *Platinamine*, and the corresponding ethyl-base contained in the salts just described, as *Platin-ethylamine* $= NH^2,C^4H^5 + NHPt,C^4H^5$. According to this view, the formula of salt *b*, is $\left.\begin{matrix}HN^2,C^4H^5\\NHPt,C^4H^5\end{matrix}\right\}HCl$, and that of the corresponding sulphate, is $\left.\begin{matrix}NH^2,C^4H^5\\NHPt,C^4H^5\end{matrix}\right\}HSO^4$. — Similarly for the corresponding methyl-compounds, VII, 317.

Chloropalladite of Ethlamine. An aqueous solution of hydrochlorate of ethylamine evaporated over the water-bath with excess of protochloride of palladium, yields large black crystals grouped in feathery tufts; by transmitted light they exhibit a fine red colour. They yield a red-brown powder, and retain their lustre unimpaired at the heat of the water-bath. (Reckenschuss, *Ann. Pharm.* 83, 343.)

			Reckenschuss.
4 C	24·0	14·11	
8 H	8·0	4·70	
2 Cl	70·8	41·62	
Pd	53·3	31·34	31·26
N	14·0	8·23	
$\left.\begin{matrix}C^4H^7N,HCl + PdCl\\\text{or } C^4H^5NCl,PdCl\end{matrix}\right\}$	170·1	100·00	

Hydrochlorate of Ethylamine with Cyanide of Mercury. Obtained by mixing a neutral solution of hydrochlorate of ethylamine with aqueous cyanide of mercury, and evaporating over the water-bath to the crystallizing point. Large, laminated crystals, which are permanent in the air, and are not decomposed by the heat of the water-bath. Soluble in water, sparingly in cold alcohol. Taste disagreeably metallic. (Kohl & Swoboda, *Ann. Pharm.* 83, 342.)

			Kohl & Swoboda.
8 C	48·0	14·40	
8 H	8·0	2·40	
Cl	35·4	10·61	
2 Hg	200·0	59·99	59·6
3 N	42·0	12·60	
$C^4H^7N,HCl + 2C^2NHg$	333·4	100·00	

Acetate of Ethylamine. When ethylamine vapour is passed into a vessel containing glacial acetic acid and surrounded with ice, the salt is obtained in the form of a very deliquescent crystalline mass of dazzling whiteness. Anhydrous phosphoric acid chars it rapidly, but does not give rise to the formation of any compound analogous to acetonitrile. (Wurtz.)

¶ Biniodethylamine. $C^4H^5I^2N$.

WURTZ. *N. Ann. Chim. Phys.* 30, 478.

Iodine introduced into an aqueous solution of ethylamine exerts an immediate action attended with rise of temperature, producing hydriodate of ethylamine, and a bluish black liquid which is biniodethylamine, (p. 58). This compound decomposes when distilled, giving off vapours of iodine, and consequently has not yet been obtained in a state of purity. — It is soluble in alcohol and ether. Caustic potash decomposes it gradually, forming iodide of potassium, a small quantity of iodate of potash, and a yellow, crystalline residue, the composition of which has not been ascertained.

				Wurtz.
4 C	24	....	8·13	..... 7·90 to 8·33
5 H	5	....	1·69	..... 1·80 „ 2·03
2 I	252	....	85·42	..... 86·38
N	14	....	4·76	
$C^4H^5I^2N$	295	....	100·00	

¶ Bibromethylamine. $C^4H^5Br^2N$.

WURTZ. *N. Ann. Chim. Phys.* 30, 477.

Bromine acts on ethylamine in the same manner as iodine, but more violently, so that it is necessary to add the bromine drop by drop, and to cool the liquid with ice. The greater part of the resulting bibromethylamine remains dissolved in the watery liquid, only a small portion settling down in the form of an oil as the action approaches its termination. The dissolved portion may, however, be extracted by agitating with ether, and evaporating the ethereal solution. — The product is an oily liquid having an orange-red colour arising from a slight excess of bromine, which, may, however, be removed by agitation with weak potash. It is heavier than water, and has a pungent odour.

¶ Bichlorethylamine. $C^4H^5Cl^2N$.

WURTZ. *N. Ann. Chim. Phys.* 30, 474.

Chlorine acts on ethylamine in the same manner as bromine and iodine, forming hydrochlorate of ethylamine and bichlorethylamine:

$$2C^4H^7N + 4Cl = C^4H^7N,HCl + C^4H^5Cl^2N + HCl.$$

The action is attended with rise of temperature, and a slight evolution of nitrogen gas.

Preparation. Washed chlorine gas is passed to saturation into a dilute solution of ethylamine, contained in a tube surrounded with ice.

The product is then deposited in the form of a yellow liquid, which may be purified by washing with water and rectifying over chloride of calcium.

Properties. Thin, mobile liquid of a light yellow colour, has a penetrating odour, and produces coughing and flow of tears. Boils at 91°. The vapour explodes when heated in a tube, but not with sufficient force to break the tube.

			Wurtz.
4 C	24·0	21·09	21·12
5 H	5·0	4·39	4·51
2 Cl	70·8	62·21	62·29
N	14·0	12·31	
$C^4H^5Cl^2N$	113·8	100·00	

Decompositions. This compound treated with excess of chlorine is converted into a solid body which crystallizes in scales. Ammonia decomposes and dissolves it gradually. Caustic potash decomposes it slowly, forming chloride of potassium, acetate of potash, and ammonia, a gas containing chlorine being also given off in small quantity, and a few drops of an oily liquid, which has a disagreeable odour like that of impure cyanide of ethyl, sinking to the bottom:

$$C^4H^5Cl^2N + 3KO + HO = C^4H^3KO^4 + NH^3 + 2KCl.$$

The gas and the oily liquid must be regarded as secondary products. (Wurtz.)

¶ Biethylamine. $C^8H^{11}N = (C^4H^4)^2, H^3N = \left.\begin{matrix} C^4H^5 \\ C^4H^5 \\ H \end{matrix}\right\} N.$

HOFMANN. *Phil. Trans.* 1850, I, 120; *Chem. Soc. Qu. J.* 3, 300.

Diethylamine, Diethylammonia, Diethylia, Biethylia.

Obtained in the form of a hydrobromate by the action of bromide of ethyl on ethylamine:

$$(C^4H^5)H^2,N + C^4H^5,Br = (C^4H^5)^2HN,HBr.$$

When an aqueous solution of ethylamine is mixed with excess of bromide of ethyl, and the mixture boiled for some hours in a sealed tube, hydrobromate of biethylamine is deposited in needle-shaped crystals. — This salt distilled with potash yields the base in the form of a very volatile and inflammable liquid, extremely soluble in water and strongly alkaline.

Chloroplatinate of Biethylamine or of *Biethylium.* — Biethylamine neutralized with hydrochloric acid and mixed with a strong solution of bichloride of platinum, yields a very soluble platinum-salt, which crystallizes in orange-red grains. (Hofmann.)

				Hofmann.
8 C	48·0	....	17·19	..... 17·33
12 H	12·0	....	4·30	..... 4·39
N	14·0	....	5·03	
3 Cl	106·2	....	38·03	
Pt	99·0	....	35·45	..... 35·45
$C^8H^{11}N,HCl,PtCl^2$ } or $C^8H^{12}N,Cl,PtCl^2$ }	279·2	....	100·00	

If ethylamine be regarded as C^4H^5N,H^2 (p. 58), biethylamine may be expressed by the formula $C^4(C^4H^5)H^4N,H^2$ or C^4AeH^4N,H^2, derived from the former by the substitution of 1 At. ethyl for 1 At. hydrogen in the nucleus.

¶ Triethylamine. $C^{12}H^{15}N=(C^4H^4)^3,H^3N=(C^4H^5)^3N$.

HOFMANN. *Phil. Trans.* 1850, I, 121; *Chem. Soc. Qu. J.* 3, 301.

Triethylammonia, Triethylia, Triethyliaque, Triæthyliak, Triæthylamin.

Obtained from biethylamine in the same manner as the latter is prepared from ethylamine.

Light, colourless, strongly alkaline liquid, very volatile and inflammable; less soluble in water than biethylamine.

The *hydrobromate* crystallizes in beautiful fibrous crystals, sometimes several inches long.

Platinum-salt. — Very soluble in water. Crystallizes on cooling from concentrated solutions in magnificent orange-red rhombic crystals, which are obtained of perfect regularity and considerable size (half an inch broad) even from very small quantities of liquid. (Hofmann.)

				Hofmann.
12 C	72·0	....	23·44	..... 23·42
16 H	16·0	....	5·21	..... 5·22
N	14·0	....	4·55	
3 Cl	106·2	....	34·57	
Pt	99·0	....	32·23	..... 32·04
$C^{12}H^{15}N,HCl,PtCl^2$ } or $C^{12}H^{16}NCl,PtCl^2$ }	307·2	....	100·00	

Triethylamine might also be regarded, similarly to biethylamine, as $C^4(C^4H^4)^2H^3N,H^2$.

¶ Tetrethylium. $C^{16}H^{20}N=(C^4H^4)^4H^4,N=(C^4H^5)^4N$.

HOFMANN. *Phil. Trans.* 1851, II, 357; *Chem. Soc. Qu. J.* 4, 304.

Tetrethylammonium. — Obtained as an iodide or bromide by the action of iodide or bromide of ethyl on triethylamine.

$$C^{12}H^{15}N + C^4H^5I = C^{16}H^{20}N,I.$$

The iodide acts quickly with the aid of heat; the bromide very slowly.

Tetrethylium is not known in the separate state.

		Calculation.	
16 C	96	.....	73·84
20 H	20	.....	15·39
N	14	.....	10·77
$(C^4H^5)^4N$	130	.....	100·00

Hydrated Oxide $(C^4H^5)^4NO,HO$. — Prepared by decomposing the iodide with oxide of silver. — The solution of the iodide is gently heated, and recently precipitated oxide of silver added in small portions, with agitation, till the resulting iodide of silver assumes a permanent yellow colour. The liquid filtered from the silver-precipitate is a solution of the hydrated oxide of tetrethylium. It may likewise be obtained by decomposing the sulphate with baryta; but this process is not so good as the preceding, on account of the difficulty of getting rid of the excess of baryta or of sulphuric acid. The alkaline solution evaporated in vacuo over sulphuric acid and lime, yields after some time, long hair-like needles which are extremely deliquescent and attract carbonic acid rapidly from the air. By remaining longer in vacuo, the crystals disappear again, and the liquid dries up to a semi-solid mass, which also deliquesces and attracts carbonic acid rapidly.

The solution of this compound is strongly alkaline, and has the pungent bitterness of quinine. In the concentrated state, it burns the tongue and acts on the epidermis like caustic potash or soda; rubbed between the fingers, it excites the well known sensation produced by the fixed alkalies, and the same peculiar odour. It saponifies fats as readily as potash, converts furfuramide into furfurine, and decomposes oxalic ether into oxalic acid and alcohol. — With metallic solutions it behaves like caustic potash, excepting that hydrate of alumina is less soluble in it, and hydrated chromic oxide quite insoluble.

A moderately concentrated solution of oxide of tetrethylium may be boiled without alteration, but at an advanced state of the evaporation, decomposition sets in, even at the temperature of the water-bath, the residue intumescing strongly, and being gradually but completely resolved into water, triethylamine, and olefiant gas:

$$C^{16}H^{20}NO,HO = 2HO + C^{12}H^{15}N + C^4H^4.$$

The solution of the oxide boiled for about 24 hours with iodide of ethyl in a flask provided with a condensing tube, so that the volatilized products may be condensed and run back, becomes perfectly neutral, and is converted into alcohol and iodide of tetrethylium:

$$C^{16}H^{20}NO,HO + C^4H^5I = C^4H^6O^2 + C^{16}H^{20}N,I.$$

A concentrated solution of the oxide mixed with an alkaline solution of iodide of potassium, yields a crystalline precipitate of iodide of tetrethylium; this effect is due to the insolubility of the latter substance in alkaline liquids (p. 67).

Salts of Tetrethylium. The oxide combines readily with acids, forming salts which are all, except the carbonate, highly deliquescent. They may be obtained either by saturating the base with the respective acids or by double decomposition. The sulphate, nitrate, phosphate, carbonate, chloride, bromide and iodide, all crystallize. — The tribasic phosphate is strongly alkaline, like the soda-salt.

Iodide of Tetrethylium. — When perfectly anhydrous iodide of ethyl is added to triethylamine dried over hydrate of potash, the mixture becomes slightly turbid, heat being evolved at the same time. The action goes on but slowly at ordinary temperatures, the mixture after several days being converted into a solid mass; but on exposing the mixture for a minute or two to the temperature of boiling water, a powerful reaction ensues; the liquid remaining for some time in a state of brisk ebullition, even after removal of the heat, and solidifying on cooling, into a hard mass of crystals, which is snow-white or yellowish, according as the triethylamine or the iodide of ethyl is in excess. To avoid loss of triethylamine, it is best to heat the mixture in sealed tubes. On dissolving the crystalline mass in cold water and leaving the solution to evaporate spontaneously, the iodide is obtained in beautiful well-defined white crystals, of considerable size, which may be separated by mechanical means from small quantities of a reddish iodine compound sometimes formed by the action of the air. This latter substance is formed in much larger quantity at higher temperatures, for which reason it is best to avoid the use of hot water in the purification. (*vid. infra.*)

The crystals are anhydrous, and do not diminish in weight by exposure to the temperature of boiling water. When rapidly heated to a higher temperature, they fuse, and are decomposed into triethylamine and iodide of ethyl, which form two layers in the receiver, but quickly unite and reproduce the original compound.

The aqueous solution mixed with caustic potash solidifies at once to a crystalline mass consisting of the iodide itself, which is less soluble in alkaline liquids than in pure water. — With nitrate or sulphate of silver, it yields iodide of silver, and a solution of nitrate or sulphate of tetrethylium. With oxide of silver it yields a solution of the hydrated oxide of tetrethylium (p. 66). (Hofmann.)

				Hofmann.
16 C	96	37·50		37·41
20 H	20	7·81		7·71
N	14	5·47		
I	126	49·22		49·28
$C^{16}H^{20}NI$	256	100·00		

Teriodide of Tetrethylium. When iodide of ethyl is heated for some time with alcoholic ammonia in such a manner that the volatilized portions may condense and run back again, a liquid is formed containing iodide of ammonium and the protiodides of the four ethyl-ammoniums; and this when exposed to the air for about a month, (whereby the iodide of ammonium is decomposed and iodine set free) yields teriodide of tetrethylium in large shining, dark-red prismatic crystals. — The same compound is more quickly obtained by heating the liquid with iodine; it then separates in small needle-shaped crystals (Weltzien, *Ann. Pharm.* 86, 292; 91, 33).

				Weltzien.		
16 C	96	18·89		18·31		17·75
20 H	20	3·94		4·58		4·50
N	14	2·76		2·76		2·02
3 I	378	74·41		74·88		74·93
$(C^4H^4)^4NI^3$	508	100·00		100·53		99·20

Teriodide of trethylium boiled with aqueous potash is partially

decomposed, giving off a volatile ethyl-base, probably triethylamine, and forming iodide of potassium, iodate of potash, and iodoform. To account for the formation of these products, however, we must suppose that carburetted hydrogens are also given off:

$$3C^{16}H^{20}NI^3 + 6KO = 3C^{12}H^{15}N + 5KI + KO,IO^5 + C^2HI^3 + C^{10}H^{14}.$$

Teriodide of tetrethylium dissolves slowly in cold water, readily in boiling alcohol; from the latter solution it crystallizes in needles arranged in feathery groups. It dissolves also in the iodides of potassium, sodium, and the ethyl-ammoniums, and separates from these solutions in large crystals. (Weltzien).

Periodide. — The liquid from which the teriodide had crystallized, yielded on dilution with water, a heavy, red-brown, oily compound, rich in iodine, and probably consisting of a higher iodide of tetrethylium. (Weltzien).

[A warm solution of iodide of tetramethylium, mixed with an alcoholic solution of iodine, yields shining crystals consisting of penta-iodide of tetramethylium $(C^2H^3)^4NI^5$; and the solution of this compound again treated with iodine yields a still higher compound, probably $(C^2H^3)^4NI^{10}$ (Weltzien).]

Bromide. White, opaque, granular crystals, obtained by acting upon triethylamine with bromide of ethyl. (Hofmann).

Iodo-mercurate. 1. Mercuric iodide boiled with a solution of iodide of tetrethylium, immediately loses its red colour and is converted into a yellow compound, which fuses and collects as a transparent layer at the bottom of the vessel. On cooling, it solidifies to a brittle mass, having a crystalline fracture. — 2. Iodide of tetrethylium mixed with a large excess of corrosive sublimate, yields a whitish crystalline precipitate which is a mixture of the iodo-mercurate with a large quantity of the corresponding chlorine-compound (*infra*):

$$6C^{16}H^{20}NI + 30HgCl = C^{16}H^{20}NI,5HgI + 5(C^{16}H^{20}NCl,5HgCl).$$

By boiling with water the latter is removed, while the iodine-compound remains behind.

			Hofmann.
$C^{16}H^{20}N$	130	9·38	
6 I	756	54·54	53·76
5 Hg	500	36·08	
$(C^4H^5)^4NI,5HgI$	1386	100·00	

Chloromercurate. On adding an excess of corrosive sublimate to a nearly neutral solution of chloride of tetrethylium, a beautiful white crystalline precipitate is formed, which is soluble in water and in hydrochloric acid, especially on boiling. From the boiling solution it is deposited on cooling, in plates which have a greasy appearance.

			Hofmann.
$C^{16}H^{20}N$.....	130·0	15·43	
6 Cl	212·4	25·21	25·05
5 Hg.....	500·0	59·36	59·01
$(C^4H^5)^4NCl,5HgCl$.	842·4	100·00	

Chloro-aurate. Lemon-yellow precipitate obtained by mixing the

solutions of the two chlorides. Dissolves but sparingly in cold water and in hydrochloric acid.

				Hofmann.
$C^{16}H^{20}N$	130·0	27·63		
4 Cl	141·6	30·09		
Au	199·0	42·28		42·00
$(C^4H^5)^4NCl,AuCl^3$	470·6	100·00		

Chloroplatinate. Bichloride of platinum added to the chloride of tetrethylium, immediately forms an orange-yellow precipitate, which in every respect resembles the corresponding potassium and ammonium-salts. Slightly soluble in water; less soluble in alcohol and ether. May be crystallized in beautiful octohedrons. (Hofmann).

				Hofmann.
16 C	96·0	28·63		28·89
20 H	20·0	5 95		6·08
N	14·0	4·20		
3 Cl	106·2	31·68		
Pt	99·0	29·54		29·27
$(C^4H^5)^4NCl,PtCl^2$	335·2	100·00		

¶ Methylotriethylium.

$C^{14}H^{18}N=(C^2H^3)(C^4H^4)^3,H^4N=(C^2H^3)(C^4H^5)^3N.$

HOFMANN. *Phil. Trans.* 1851, II, 373; *Chem. Soc. Qu. J.* 4.

Methylotriethylammonium. — Obtained as an iodide by the action of iodide of methyl on triethylamine:

$$(C^4H^5)^3N + C^2H^3I = (C^2H^3)(C^4H^5)^3N,I.$$

The mixture of the two liquids solidifies to a crystalline mass of iodide of methylotriethylium, slowly at ordinary temperatures, instantly on boiling. The iodide resembles iodide of tetrethylium, and is extremely soluble, forming a neutral, very bitter solution, which is decomposed by potash, the iodide being precipitated without alteration.

The iodide decomposed by oxide of silver yields the hydrated oxide, which dries up in vacuo to a crystalline compound, resembling the hydrated oxide of tetrethylium.

Platinum-salt. — Obtained as a beautiful crystalline precipitate by adding bichloride of platinum to a solution of the base saturated with hydrochloric acid.

				Hofmann.
14 C	84·0	26·15		
18 H	18·0	5·60		
N	14·0	4·36		
3 Cl	106·2	33·07		
Pt	99·0	30·82		30·48
$C^{14}H^{18}NCl,PtCl^2$	321·2	100·00		

The base forms crystalline salts with sulphuric, hydrochloric, nitric, and oxalic acid. (Hofmann.)

¶ *Conjugated Compounds containing Arsenic: Arsenethyls.*

LANDOLT. *Ann. Pharm.* 89, 301, *Chem. Gaz.* 1854.

These compounds are obtained by the action of iodide of ethyl on arsenide of sodium. They are three in number, viz. *Arsenbiethyl* or *Vinocacodyl* $(C^4H^4)^2AsH^2 = (C^4H^5)^2As$: *Arsentriethyl*, $(C^4H^4)^3AsH^3 = (C^4H^5)^3As$; and *Arsenethylium* $(C^4H^4)^4AsH^4 = (C^4H^5)^4As$. This last is analogous to tetrethylium, stibmethylium, &c.

Preparation. 1. Arsenide of sodium prepared by the direct combination of its elements* is finely pounded, together with 4 or 5 times its weight of quartz-sand (if pulverized alone it takes fire); the mixture introduced into a number of small short-necked flasks (holding about 3 oz.), so as to fill them to about two-thirds; iodide of ethyl added to the contents of one of the flasks (the others being well corked up); and the flask immediately connected with a condensing apparatus through which a stream of carbonic acid is passed during the whole operation. This condensing apparatus (which is the same as that used by Löwig and Schweizer in the preparation of stibethyl, p. 78), consists of a tall wide cylindrical vessel closed by a cork having three apertures. Through one of these apertures passes a tube proceeding from the carbonic acid apparatus and reaching to the bottom of the vessel; through the second, a short straight tube to carry that gas off; and through the third is inserted the distillation-tube connected with the flask containing the mixture. Within the glass cylinder are placed two small bottles, into one of which the lower end of this conducting tube is inserted. The mixture of iodide of ethyl and arsenide of sodium soon becomes so hot that a large portion of the iodide of ethyl distils over spontaneously; as soon as this action is over, the flask is removed, more iodide of ethyl poured in, and the same operation repeated as long as any action takes place. The final residue of iodide of ethyl is expelled by gently heating the flask, and on subsequently applying a stronger heat, the arsenides of ethyl distil over. The cork of the cylindrical vessel must then be raised, together with the tubes, the vessel turned round so as to bring the end of the distillation-tube over the second bottle, and the vessel again closed as before. The exact moment for changing the bottles may be known by the conducting tube, which has previously been hot and dry, becoming cold and wetted with drops of liquid. The heat is then gradually raised

* Pure metallic arsenic, in the state of fine powder, is gently heated in a furnace having a good draught, till it begins to fume, and small pieces of sodium introduced from time to time till the mixture begins to assume a fluid consistence, which effect takes place when a quantity of sodium has been introduced, about equal to that of the arsenic. As the product is highly combustible, it is necessary to exclude the air as completely as possible during the whole operation. For this purpose, the arsenic is placed in a porcelain crucible, enclosed within a hessian crucible, both being provided with closely fitting covers, which must only be removed to introduce the sodium, or to stir the mixture with an iron rod, so as to ensure uniform combination. The action is very violent, and attended with vivid incandescence, portions of the mixture being sometimes thrown out. The alloy, which has a crystalline fracture and silver-white colour, must be kept in closely stoppered bottles filled up with quartz-sand. It decomposes water with evolution of arseniuretted hydrogen, an effect which takes place even in damp air; hence it must be handled with caution.

to redness; and when nothing more passes over, the flask is removed, a second put in its place, and the whole series of operations repeated. The contents of 12 or 15 flasks, requiring about a pound of iodide of ethyl, yield about 2 oz. of the mixed arsenides of ethyl. — At the end of the operation, the first bottle contains iodide of ethyl mixed with a small quantity of the arsenides; the second, a nearly colourless liquid, frequently mixed with a red substance. This liquid — which is heavier than water, has an intolerable odour, excites a copious flow of tears, fumes strongly in the air, and afterwards takes fire, — is a mixture of *arsenbiethyl* and *arsentriethyl*. — These two compounds may be separated by fractional distillation, the latter being much the more volatile of the two. For this purpose, the crude product is transferred, within an atmosphere of carbonic acid, into a small flask, and the flask immediately connected with the distillation-tube of the condensing apparatus above described, a number of small bottles being previously arranged within the large cylindrical vessel, so that by turning the vessel, each of them may be successively brought beneath the extremity of the distillation-tube. The flask is heated in a small sand-bath, and a rapid current of carbonic acid gas passed through the apparatus during the whole operation. In one experiment, the first portions of the distillate, which passed over between 60° and 138°, contained iodide of ethyl, and solidified after a while into a mass of crystals consisting of *iodide of arsenethylium*, Ae^4AsI. The second portion, which was collected at 140°, still contained iodine; the third, which passed over between 140° and 185°, consisted of pure arsentriethyl; afterwards a mixture of that compound with arsenbiethyl distilled over; while pure arsenbiethyl together with a little metallic arsenic, remained in the flask. This process is best adapted for the preparation of arsentriethyl, which it yields in much larger quantity than arsenbiethyl. The latter is more advantageously obtained by the following process:

2. Arsenide of sodium is treated with excess of iodide of ethyl as before; the product digested with ether; the ethereal extract, which contains arsenbiethyl, arsentriethyl, and iodide of ethyl, mixed with absolute alcohol; the ether distilled off; and the alcoholic solution mixed with water, which precipitates arsenbiethyl, and dissolves iodide of arsenethylium formed by the action of the iodide of ethyl on arsentriethyl. — The treatment of the arsenide of sodium with iodide of ethyl is performed in small flasks as in the first process, and the iodide of ethyl, which distils over in consequence of the heat generated by the reaction, is collected in a small flask, and subsequently poured back again, together with fresh iodide of ethyl, these operations being repeated as long as any action continues; the transference of the liquid must be effected as quickly as possible to avoid access of air. When the action is over, the greater part of the remaining iodide of ethyl must be distilled off by a gentle heat, sufficient however being left to keep the mixture moist; if the excess were all removed, the final product would consist of a mixture of arsenbiethyl and arsentriethyl, which would then require fractional distillation to separate them. When the contents of 10 or 12 flasks have been thus treated, the whole is transferred into a bottle containing from 1½ to 2 pounds of ether, and previously filled with carbonic acid; the bottle tightly closed and well shaken; the contents left to stand till the liquid has become clear; this liquid decanted into another bottle filled with carbonic acid, (whereupon it generally becomes turbid, and

deposits a yellow powder, the quantity of which is greater, the longer the liquid has been exposed to the air during the several operations); the residue again treated with ether; and this treatment repeated as long as a drop of the ethereal extract becomes turbid on exposure to the air. The whole of the ethereal extract is then mixed with absolute alcohol, and the ether quickly distilled off. During this distillation, the yellow powder just mentioned cakes together, and forms a red, resinous body, melting at 70°, and insoluble in all reagents.

The alcoholic solution is next transferred, in an atmosphere of carbonic acid, into a cylindrical glass vessel capable of being well closed, and mixed with water free from air till it becomes very turbid. It is left to stand till it becomes clear, and an oily body separates out; then decanted from this oil into another vessel, and a large quantity of water added, whereupon arsenbiethyl is separated in the form of an oily liquid, having a faint greenish yellow colour and powerful odour. It is decanted into a small bottle; freed from the supernatant liquid by means of a pipette; and preserved under a layer of de-areated water. — In all these operations, the greatest care must be taken to exclude the air; otherwise a red powder forms, which mixes with the radical and renders its purification very difficult.

The water used for precipitating the arsenbiethyl contains *iodide of arsenethylium*, together with other arsenical compounds, which have not yet been separated one from the other. On agitating the watery liquid with ether, a portion of these compounds dissolves, together with a considerable quantity of iodide of arsenethylium, although this compound is by itself but sparingly soluble in ether; and on leaving the liquid to evaporate in the air, there remains a yellow syrup, from which, after a while, the iodide of arsenethylium crystallizes in beautiful prismatic crystals. It may be separated from the liquid compounds which adhere to it, by washing with a small quantity of water, and obtained in a state of purity by several recrystallizations from water.—The watery solution after being treated with ether as above, still contains a small quantity of iodide of arsenethylium, which may be crystallized by evaporation over the water-bath, but it is very impure.

The residue in the flasks in which arsenide of sodium has been treated with iodide of ethyl, and the product digested with ether (p. 71), still contains a number of arsenical organic compounds, among which the *oxide of arsentriethyl*, Ae^3AsO^2, exists in considerable quantity. It may be separated by treating the residue with absolute alcohol, evaporating the alcoholic extract, and subjecting it to dry distillation. The oxide then passes over in the form of a yellow oily liquid.

¶ Arsenbiethyl or Vinocacodyl. $(C^4H^4)^2,AsH^2=(C^4H^5)^2As$.

Diarsenide of Ethyl, Ethylo-cacodyl. — For the preparation, *vid.* p. 71.

Properties. Oily liquid, having a faint yellowish colour, strong refracting power, and a very disagreeable, pungent, alliaceous odour. Heavier than water; in which it sinks without mixing. Boils between 185° and 190°.

				Landolt (*mean*).
8 C	48	....	36·09	..... 35·73
10 H	10	....	7·52	..... 7·75
As	75	....	56·39	..... 56·92
$(C^4H^5)^2As$	133	....	100·00	

According to Gmelin's nucleus-theory, this compound should be regarded as belonging to the eight-carbon series, and as a conjugated compound of 1 At. H. with the secondary nucleus C^8ArH^7, formed from the primary nucleus C^8H^8, by the replacement of 1 At. H by Ar = AsH^2; according to this view, its formula would be C^8ArH^7,H. (Vid. *Cacodyl.*)

Arsenbiethyl rapidly absorbs oxygen from the air, and generally breaks out into a dull flame, giving off vapours of arsenious acid. In this respect, however, its properties vary according to the mode of preparation. A drop of the product obtained by the first method (p. 70), takes fire immediately when let fall upon wood or paper; but with that which is obtained by the second method (p. 71), this effect does not take place till the temperature is raised to 180°. — Strong nitric acid oxidizes it rapidly, with evolution of light and heat. Dilute nitric acid likewise oxidizes it, but less completely, a red substance analogous to Bunsen's erythrarsin, being formed as a secondary product. This red body, which is likewise formed when arsenbiethyl is incompletely burned in the air, is light red when first produced, but soon becomes darker, and when dry forms a brown powder, which turns white by continued exposure to the air; it is insoluble in water, alcohol, and ether; heated on platinum-foil it burns away completely with a pale arsenic-flame; heated in a test-tube it gives off inflammable vapours, having an unpleasant odour, and leaves a considerable quantity of arsenic. — Strong sulphuric acid has no action on arsenbiethyl at ordinary temperatures, but evolves sulphurous acid when heated with it; dilute sulphuric acid does not affect it. — Arsenbiethyl reduces the noble metals from their solutions; its alcoholic solution added to a solution of nitrate of silver or corrosive sublimate immediately throws down metallic silver or mercury. This character, and the production of the red powder above mentioned, distinguish arsenbiethyl from the other arsenides of ethyl.

Combinations. Arsenbiethyl combines directly with sulphur and with the halogen-radicals, the combination being attended with great evolution of heat. All its compounds hitherto obtained are liquids, and distinguished by a peculiarly repulsive and persistent odour, which excites a copious flow of tears; continued exposure to this odour produces sneezing, persistent catarrh, and head-ache. — The compounds contain 1 At. arsenbiethyl with 1 At. O, S, Cl, &c.

Iodide of Arsenbiethyl. Obtained by saturating an ethereal solution of arsenbiethyl with an ethereal solution of iodine, and evaporating the mixture out of contact of air; (Landolt); also by dry distillation of the compound $(C^4H^5)^4AsI,AsI^3$ (Cahours & Riche, p. 78).—Yellow oil, readily soluble in alcohol and ether, but not miscible with water. Does not fume in the air, but burns slowly when heated, giving off vapours of iodine. (Landolt.) Distilled with zinc-amalgam it yields arsenbiethyl. (Cahours & Riche.)

Decomposed by sulphuric and nitric acid, with separation of iodine. The alcoholic solution mixed with nitrate of silver, forms an immediate precipitate of iodide of silver, but gives no precipitate with a solution of

corrosive sublimate in dilute alcohol. (Landolt.) With sulphate and nitrate of silver, it yields iodide of silver and crystallized *sulphate* or *nitrate of arsenbiethyl*. (Cahours & Riche.)

				Landolt.
8 C	48	18·53		18·90 to 19·34
10 H	10	3·86		4·13 „ 4·73
As	75	28·96		
I	126	48·65		48·45 „ 49·13
$(C^4H^5)^2AsI$	259	100·00		

Arsenbiethyl is insoluble in *water*; but dissolves readily in *alcohol* and *ether*, and is precipitated from its alcoholic solution by water.

¶ Arsentriethyl. $(C^4H^4)^3AsH^3=(C^4H^5)^3As$.

This compound is most advantageously obtained by the first method (p. 70); it passes over in a state of purity between 140° and 180°.

Properties. Colourless, very mobile liquid, having great refracting power and a disagreeable odour, like that of arseniuretted hydrogen gas. Sp. gr. 1·151 at 16·7°. Under a pressure of 736 mm. it begins to boil at 140°; but the boiling point slowly rises to 180°, a small quantity of metallic arsenic separating at the same time. Hence the compound appears to decompose in boiling. — The quantity thus decomposed is, however, very small, several portions collected between 140° and 170° not exhibiting a difference of more than 1 per cent. in the amount of carbon. — Vapour-density 5·2783.

				Landolt.
12 C	72	44·44		43·21 to 44·03
15 H	15	9·26		9·41 „ 9·88
As	75	46·30		
$(C^4H^5)^3As$	162	100·00		

	Vol.	Density.	Or:	Vol.	Density.
C-vapour	12	4·9920			
H-gas	15	1·0395	Ethyl-vapour	3	6·0315
As-vapour	½	5·1997	As-vapour	½	5·1997
Vapour of Ae^3As	2	11·2312	Vapour of Ae^3As	2	11·2312
	1	5·6156		1	5·6156

Decompositions. Arsentriethyl fumes and becomes heated when exposed to the air, but seldom takes fire unless it is gently heated; the products of the combustion are arsenious acid, carbonic acid, and water. Oxidation takes place slowly even when the compound is kept under water, in a tightly closed vessel; when it has advanced a certain stage, the liquid no longer fumes in the air. — Strong nitric acid oxidizes it rapidly, with vivid combustion and explosion; but nitric acid of sp. gr. 1·42 dissolves it slowly, with evolution of nitric oxide, and forms nitrate of arsentriethyl; no red compound analogous to erythrarsin is formed, either by the action of nitric acid or by oxidation in the air. — Arsentriethyl mixes with oil of vitriol, and on the application of heat, reduces

it to sulphurous acid. It does not reduce the oxides of the noble metals.

Combinations. Arsentriethyl combines with oxygen, sulphur, chlorine, &c., forming compounds containing 1 At. of the radical and 2 At. of the other body, analogous therefore to the compounds of stibmethyl, stibethyl, &c.

Oxide. When an ethereal solution of pure arsentriethyl is left to evaporate slowly in contact with the air at ordinary temperatures, the oxide remains in the form of a nearly colourless, oily liquid, having a slight alliaceous odour. As thus obtained, however, it is not pure, being mixed with other compounds not yet examined. — *Preparation.* The mass obtained by treating arsenide of sodium with iodide of ethyl is exhausted first with ether, and afterwards with absolute alcohol, the alcoholic extract evaporated, and the residue subjected to dry distillation in a retort (p. 72).

Oily liquid having a slight yellowish colour; heavier than water and not miscible with it; dissolves readily in alcohol and ether, and is precipitated from the alcoholic solution by water, in its original state.

The alcoholic solution has no action on litmus-paper, and does not precipitate nitrate of silver. The oxide is readily dissolved by dilute nitric acid, but is insoluble in dilute sulphuric and hydrochloric acid.

				Landolt.
12 C	72	40·45		39·58 to 40·38
15 H	15	8·43		8·73 ,, 9·29
As	75	42·13		43·17
2 O	16	8·99		
$(C^4H^5)^3AsO^2$	178	100·00		

This compound becomes turbid on exposure to the air, and passes to a higher state of oxidation, but without fuming or inflammation.

When pure arsentriethyl is left to stand for some time in a loosely stoppered bottle, very fine tabular crystals gradually form on the surface; and if the crust thus formed be now and then broken and pushed to the bottom, the entire liquid may be converted into a solid compound. The crystals are quite inodorous, and dissolve in alcohol and ether; but in contact with water, they deliquesce to a colourless oil which remains quite undissolved; deliquescence likewise takes place in a moist atmosphere, and on exposure to a gentle heat. This compound has an acid reaction; its alcoholic solution forms with nitrate of silver a yellow flocculent precipitate which shrinks up greatly in drying, and forms a brown powder containing 60·8 p.c. of silver.

Sulphide. — 1. When an ethereal solution of arsentriethyl is boiled with washed flowers of sulphur, the liquid decanted into another vessel as soon as the excess of sulphur has settled down, and left to cool, the sulphide of arsentriethyl separates out in prismatic crystals; if, however, too much ether has been used, the crystals do not form till the liquid is evaporated. The crystals are generally contaminated both with sulphur and with oxide of arsentriethyl, which latter is very difficult to remove. They are best purified by recrystallization from alcohol or water, the

compound then separating in small feathery crystals; larger crystals may be obtained by redissolving in warm ether, and leaving the solution to evaporate slowly. — 2. The compound may likewise be obtained by boiling an aqueous solution of pentasulphide of potassium with oxide of arsentriethyl; crystals of the sulphide then separate on cooling. — The compound has a bitter taste, but is quite inodorous when pure.

			Landolt.
12 C	72	37·11	
15 H	15	7·73	
As	75	38·66	
2 S	32	16·50	16·17 — 15·77
$(C^4H^5)^3AsS^2$	194	100·00	

Sulphide of arsentriethyl is not altered by exposure to the air. — Heated in a test tube, it melts somewhat below 100°, forming a yellowish oily liquid which boils at a higher temperature, giving off spontaneously inflammable vapours, and covering the inside of the tube with a yellowish red deposit of sulphide of arsenic. — When boiled with potash-ley, it is not decomposed, but merely melts, and solidifies in a crystalline mass on cooling. — Strong nitric acid acts very powerfully on it, converting the sulphur into sulphuric acid, and partially oxidizing the arsentriethyl. — Dilute hydrochloric acid decomposes it imperfectly, giving off sulphuretted hydrogen, and forming a small quantity of arsentriethyl, which may be recognized by its pungent odour. — The aqueous solution forms with nitrate of silver, a black precipitate of sulphide of silver; no precipitate with acetate of lead or with copper salts. With mercurous nitrate, it forms a black precipitate which soon turns white; with corrosive sublimate, a bulky white precipitate.

Sulphide of arsentriethyl dissolves readily warm water and in boiling ether, but is nearly insoluble in cold ether.

Iodide of Arsentriethyl. — When an ethereal solution of iodine is added to an ethereal solution of arsentriethyl, as long as decoloration takes place, iodide of arsentriethyl separates in large quantity as a sulphur-yellow flocculent precipitate. It is immediately separated from the liquid, washed with a small quantity of ether, pressed between paper, dried at a very gentle heat, and then enclosed in a tight-stoppered bottle. It is also obtained by dry distillation of the compound $(C^4H^5)^4AsI, AsI^3$. (Cahours & Riche. p. 78). — Very instable; when exposed to the air, if only for a short time, it turns brown and soon deliquesces to a dark-coloured syrupy liquid; even when completely protected from the air, it gradually assumes a brown colour. When heated in a test-tube, it assumes a darker colour, and fuses at 160° to a brown liquid, which solidifies again on cooling; at 190° it is converted, with partial decomposition, into vapour which condenses on the colder parts of the tube in light yellow drops; no separation of iodine appears to take place. Nitric and sulphuric acid decompose it immediately, with separation of iodine; it dissolves in hydrochloric acid when heated, but separates out again unchanged on cooling. Strong potash-ley dissolves out the iodine, and forms oxide of arsentriethyl. Distilled with zinc-amalgam, it yields arsentriethyl. (Cahours & Riche).

Iodide of arsentriethyl dissolves readily in water and alcohol, but sparingly in ether. The aqueous solution forms with nitrate of silver an

immediate precipitate of iodide of silver; from acetate of lead it separates iodide of lead. With corrosive sublimate it forms a white precipitate soluble in excess.

			Landolt.
12 C	72	17·39	17·68
15 H	15	3·62	4·14
As	75	18·12	
2 I	252	60·87	60·64
$(C^4H^5)^3AsI^2$	414	100·00	

Chloride. — Not yet obtained in a definite state. When an alcoholic solution of oxide of arsentriethyl is mixed with strong hydrochloric acid, and water afterwards added, the oxide separates out unaltered, but the liquid at the same time acquires an intolerable odour and emits a vapour which attacks the eyes strongly. This odour is altogether foreign to the oxide of arsentriethyl, and is therefore probably due to the formation of a small quantity of chloride.

Nitrate. — Obtained by treating arsentriethyl or its oxide with dilute nitric acid. On evaporating the liquid over the water-bath, a thick syrup is obtained; and this, when left for some time over sulphuric acid, deposits crystals, which on exposure to the air, rapidly absorb water and deliquesce. (Landolt.)

¶ Arsenethylium. $(C^4H^4)^4AsH^4=(C^4H^5)^4As$.

Formed, as an iodide, by the action of iodide of ethyl on arsentriethyl:

$$(C^4H^5)^3As + C^4H^5I = (C^4H^5)^4As,I.$$

Also by the action of metallic arsenic on iodide of ethyl. (Cahours & Riche, p. 78).

Not known in the free state.

	Calculation.	
16 C	96	50·26
20 H	20	10·47
As	75	39·27
$(C^4H^5)^4As$	191	100·00

The compounds of arsenethylium are analogous to those of potassium, ammonium, tetrethylium, stibmethylium, &c. The hydrated oxide is a fixed base resembling hydrate of potash. The salts dissolve readily in water, crystallize readily and possess great stability, undergoing no change on exposure to the air; they are inodorous, have a bitter taste, and do not appear to be poisonous. In these respects, they differ remarkably from the compounds of arsenbiethyl and arsentriethyl.

Oxide. — Obtained by the action of oxide of silver on an aqueous solution of iodide of arsenethylium. On filtering from the iodide of silver and evaporating the solution, the air being excluded as much as

possible, the hydrated oxide remains in the form of a white mass, which has a strong alkaline reaction, and quickly absorbs water and carbonic acid from the air. It is a strong base, separating ammonia from its salts at ordinary temperatures, and precipitating the earths and heavy metallic oxides from their solutions.

Iodide. — When iodide of ethyl is mixed with arsentriethyl, combination generally takes place in a few hours, the entire liquid solidifying in a mass of crystals. For the preparation, *vid.* pp. 71, 72. — Large colourless crystals, which often become somewhat darker by long keeping. They dissolve readily in water and alcohol, but are insoluble in ether and in alcohol containing ether. Nitric acid separates iodine; so likewise does sulphuric acid, with evolution of hydriodic and sulphurous acids. The crystals fall to powder when heated, giving off vapours which take fire in the air, and yielding a sublimate of metallic arsenic, but only a small quantity of iodine or iodide of arsenic.

			Landolt.	
			a.	*b.*
16 C	96	30·28	28·77	
20 H	20	6·31	6·84	
As	75	23·66		
I	126	39·75	39·09	39·85
$(C^4H^5)^4AsI$	317	100·00		

a was obtained by method 1, page 71; *b* by method 2, page 72.

Iodide of Arsenethylium with Teriodide of Arsenic $(C^4H^5)^4AsI, AsI^3$. — Obtained by heating iodide of ethyl to 200° in contact with metallic arsenic:

$$4(C^4H^5)I + 2As = (C^4H^5)^4AsI, AsI^3.$$

Splendid red tables which are decomposed by distillation, yielding iodide of arsentriethyl and iodide of arsenbiethyl. (Cahours & Riche, *Compt. rend.* 39, 546.)

Chloride. — Obtained by saturating a solution of the oxide with dilute hydrochloric acid; on evaporating the liquid under the air pump, crystals are obtained which contain 8 At. water of crystallization and deliquesce rapidly in the air. When heated, they first melt in their water of crystallization, and then gradually give it off, undergoing decomposition at the same time, and ultimately disappearing altogether, with formation of volatile products. Strong sulphuric acid decomposes the salt immediately, with evolution of hydrochloric acid gas. — The crystals dissolve readily in water and alcohol, but are insoluble in ether. The aqueous solution immediately precipitates chloride of silver from the nitrate, and forms an insoluble double salt with protochloride of mercury.

			Landolt.	
16 C	96·0	32·16		
20 H	20·0	6·70		
As	75·0	25·13		
Cl	35·4	11·89	11·88	11·98
8 HO	72·0	24·12		
$(C^4H^5)^4AsCl + 8Aq$	298·4	100·00		

Sulphate. — Obtained by precipitating iodide of arsenethylium with a solution of sulphate of silver containing excess of sulphuric acid. The liquid, when filtered and evaporated, leaves granular crystals, which may be purified by repeated crystallization. This salt dissolves readily in water and alcohol, sparingly in ether. Its taste is sour at first, afterwards bitter. Heated in a tube, it fuses with decrepitation at first, and then gives off acid vapours which do not take fire in the air.

				Landolt.
16 C	96	33·33		33·05
20 H	20	6·94		7·55
As	75	26·04		
O	8	2·78		
2 SO^3	80	27·78		28·25
HO	9	3·13		
$(C^4H^5)^4As, H\}2SO^4$	288	100·00		

Conjugated Compounds containing Antimony.

¶ Stibethyl. $(C^4H^4)^3SbH^3 = (C^4H^5)^3Sb$.

Löwig & Schweizer. *Mittheilungen der Züricher naturf. Gesellschaft.* Nr. 45 u. 51; *Ann. Pharm.* 75, 315, 327; *J. pr. Chem.* 49, 385; 50, 321; *Pharm. Centr.* 1850, 230, 536, 545; *Pogg.* 8, 338; *Arch. ph. nat.* 13, 29; 14, 288; *Instit.* 1850, 172; 1851, 30; *Laur. & Gerh. C. R.* 1850, 237, 389; *Chem. Gaz.* 1850, 201, 372, 395, 420; *Jahresber.* 1850, 470; *Chem. Soc. Qu. J.* 5, 69.

Löwig. On some compounds of Stibethyl. *J. pr. Chem.* 60, 352; *Ann. Pharm.* 88, 323.

Formation. By the action of iodide, bromide, or chloride of ethyl on antimonide of potassium.

Preparation. Antimonide of potassium prepared by igniting crude tartar with antimony,* is triturated with two or three times its weight of quartz-sand; the mixture introduced into a number of small flasks, as in the preparation of the arsenides of ethyl (p. 70), and moistened with iodide of ethyl. The action begins in a few minutes, and is attended with a rise of temperature sufficient to volatilize the excess of iodide of ethyl, which may be collected by itself in a small receiver. This action being over, the flask is connected as quickly as possible with the condensing apparatus described on page 70, and heated, gently at first, but afterwards more strongly, as long as any liquid distils over, a stream of carbonic acid gas being passed through the apparatus during the whole operation. The flask is then removed, and the distillation-tube stopped with wax till a second flask is ready, upon which the operation is

* 5 pts. of crude tartar and 4 pts. of antimony are slowly heated in a covered crucible till the tartar becomes charred; the heat then raised to whiteness for an hour; the furnace closed air-tight, and the mixture left to cool slowly. The product is a crystalline regulus containing 12 per cent. of potassium, which decomposes water rapidly, oxidizes but slowly in the air in the compact state, but becomes heated and takes fire when rubbed to powder; this effect may, however, be prevented by mixing the alloy with 2 or 3 parts of quartz-sand.

repeated. The contents of 20 to 24 flasks of 3 or 4 ounces capacity, yield 4 or 5 ounces of crude product, which may thus be obtained in the course of a day. The receiver in which the distillate has been collected is then closed, while still immersed in the atmosphere of carbonic acid, afterwards removed, and used as a retort in the rectification of the product, the same condensing apparatus being used as before. The first portions of the rectified product contain iodine, and deposit after a while a number of colourless crystals [iodide of stibethylium]. (Löwig & Schweizer.)

Properties. Transparent, colourless, mobile, strongly refracting liquid, having a disagreeable alliaceous odour. Sp. gr. 1·3244 at 16°. Does not solidify at 29°. Boils at 158·5° (bar. at 730 mm.). Vapour-density = 7·44.

				Löwig & Schweizer.
12 C	72	33·33		32·74 to 34·47
15 H	15	6·94		6·99 ,, 7·28
Sb	129	59·73		58·77 ,, 60·22
$(C^4H^5)^3Sb$	216	100·00		

Löwig & Schweizer regard stibethyl as a radical containing 2 At. ethyl united with the copula C^4H^5,Sb, and consider that the occurrence of 2 At. ethyl in it explains the combination of 1 At. stibethyl with 2 At. oxygen, chlorine. Cacodyl, C^4H^6As, on the contrary, they regard as 1 At. methyl united with the copula C^2H^3,As: hence 1 At. cacodyl combines with only 1 At. oxygen, &c. — Laurent & Gerhardt (*Comptes mensuels*, 1850, 399) supposed that the so-called stibethyl-salts contained a base $C^{12}H^{13}Sb$, to which they gave the name of stibethine, the chloride being $C^{12}H^{13}Sb,2HCl$, the nitrate $C^{12}H^{13}Sb,2HNO^6$, &c. But Gerhardt in his recent *Traité de Chimie organique*, 1, 369, regards stibethyl as $(C^4H^5)^3Sb$.

A drop of stibethyl exposed to the air at the end of a glass rod, emits thick white fumes, and in a few seconds takes fire and burns with a white, strongly luminous flame. When introduced in a thin stream into oxygen gas, it burns with dazzling brightness. But if it be made to run into a glass globe containing air, in such a manner as not to take fire, it gives off dense white fumes, which collect on the sides of the vessel in the form of a powder, which is insoluble in ether, but dissolves in alcohol and water; at the same time a transparent, colourless, viscid mass is formed, which is soluble in ether. This latter substance is the *oxide of stibethyl*, Ae^3SbO^2; the powder is *antimonite of stibethyl*, $Ae^3SbO^2,2SbO^3$. [It was originally regarded by Löwig and Schweizer as ethylostibylic acid C^4H^5Sb,O^2]. Stibethyl oxidizes very slowly when immersed in water; hence it is best to keep it under that liquid. — *Sulphur*, *selenium*, *iodine*, *bromine*, and *chlorine* combine directly with stibethyl, the action being always attended with evolution of heat, and in the case of bromine and chlorine, with inflammation. The compounds, like the oxide, all contain 1 At. stibethyl, with 2 At. of the other body, in which respect they resemble the compounds of stibmethyl (VII, 322) and arsentriethyl (p. 75). Stibethyl introduced into *hydrochloric acid gas*, yields chloride of stibethyl and free hydrogen:

$$Ae^3Sb + 2HCl = Ae^3SbCl^2 + H^2.$$

The same reaction takes place with fuming hydrochloric acid. — Dilute *nitric acid* with the aid of heat, acts on stibethyl in the same manner as on the metals, evolving nitric oxide and forming nitrate of stibethyl. — Neither fuming nitric acid nor aqua-regia oxidizes the antimony completely.

Oxide of Stibethyl, Ae^3SbO^3. — 1. Formed by the direct oxidation of stibethyl, either in the free state as above mentioned, or dissolved in alcohol or ether; as thus obtained, however, it is always more or less mixed with antimonite of stibethyl, especially when obtained from the ethereal solution. The alcoholic solution on the contrary yields but a small quantity of antimonite. Accordingly, the oxide may be obtained by leaving a dilute alcoholic solution to evaporate slowly in a loosely covered foot-glass; treating the residue with ether, which dissolves the oxide and leaves the antimonite; and repeating this treatment as long as the ether leaves any insoluble residue. — 2. The oxide may also be obtained by treating an aqueous solution of sulphate of stibethyl with baryta-water; evaporating the filtrate over the water-bath; exhausting the residue with alcohol, which dissolves out a compound of oxide of stibethyl and baryta; precipitating the baryta by carbonic acid; and evaporating the filtered alcoholic solution. — 3. From the nitrate in a similar manner. — 4. An alcoholic solution of stibethyl shaken up with finely divided red oxide of mercury, quickly reduces the mercury to the metallic state, and yields pure oxide of stibethyl.

Oxide of stibethyl in its purest state, is a transparent, colourless, viscid, amorphous mass, which dissolves readily in water and alcohol, somewhat less readily in ether; has a very bitter taste; does not appear to be poisonous; is not altered by exposure to the air; is not volatile; but when heated in a tube, gives off white vapours which burn with a bright flame, and leaves a residue containing antimony and charcoal. It is decomposed by potassium, at a gentle heat, with separation of stibethyl. Fuming nitric acid decomposes it, with evolution of light and heat; dilute nitric and strong sulphuric acid dissolve it, forming salts of stibethyl; hydrochloric acid and other hydrogen-acids dissolve it in the form of chloride of stibethyl and similar compounds. Sulphuretted hydrogen has no perceptible action upon it; but on evaporating a solution of the oxide saturated with the gas, crystals of sulphide of stibethyl are obtained; the smallest trace of antimonite of stibethyl mixed with the oxide is detected by the formation of a yellow precipitate.

Calculation.

12 C	72		31·04
15 H	15		6·46
Sb	129		55·60
2 O	16		6·90
$(C^4H^5)^3SbO^2$	232		100·00

The composition was determined by the analysis of the sulphate and nitrate.

Sulphide. Formed, with evolution of heat, when sulphur and stibethyl are brought together under water. It is however most readily obtained by boiling an ethereal solution of stibethyl with pure flowers of sulphur; the liquid decanted from the sulphur soon solidifies in needle-shaped crystals, which may be purified by leaving the adhering sulphur to oxidize in the air, and crystallizing several times from ether.

Sulphide of stibethyl thus purified forms a bulky crystalline mass having a silvery lustre, an unpleasant odour, and a bitter taste; it is permanent in the air when dry; melts above 100°; and is decomposed at a stronger heat, with formation of a liquid product resembling sulphide of ethyl. In the fused state it is decomposed by potassium, with evolu-

tion of vapours of stibethyl. The aqueous solution of sulphide of stibethyl precipitates metals from their solutions in the form of sulphides, and yields sulphuretted hydrogen with dilute acids.

				Löwig & Schweizer.
12 C	72	....	29·03	..... 29·09
15 H	15	....	6·05	..... 6·24
Sb	129	....	52·01	
2 S	32	....	12·91	..... 13·05
$(C^4H^5)^3SbS^2$	248	....	100·00	

Sulphate. — May be obtained by the direct union of its components, but more readily by decomposing sulphide of stibethyl with an exactly equivalent quantity of cupric sulphate. The filtered solution evaporated to a syrup yields perfectly white crystals, which may be dried between paper and afterwards over oil of vitriol. Excess of sulphuric acid prevents the crystallization, but does not decompose the oxide of stibethyl. — The salt is inodorous, but has a bitter and very persistent taste. The crystals suffer no loss of weight at 100°, but at a somewhat higher temperature, they become soft and melt into a colourless liquid. The salt is very soluble in water, dissolves with tolerable facility in alcohol, but is nearly insoluble in ether. Hydrochloric acid added to the aqueous solution, immediately forms a precipitate of chloride of stibethyl. Soluble baryta salts throw down the sulphuric acid.

				Löwig & Schweizer.
12 C	72	....	23·08	
15 H	15	....	4·81	
Sb	129	....	41·34	
2 O	16	....	5·13	
$2\,SO^3$	80	....	25·64	..... 24·45 .... 25·58
$(C^4H^5)^3SbO^2,2SO^3$	312	....	100·00	

Selenide. — Prepared like the sulphide, and similar to that compound in its properties, excepting that when exposed to the air, it decomposes rapidly, with separation of selenium.

Iodide. — Iodine and stibethyl combine together under water, the combination being attended with rise of temperature. On adding iodine to an ethereal solution of stibethyl, a violent momentary ebullition takes place and the iodine quickly disappears. The compound is however most easily prepared by adding iodine by small portions to an alcoholic solution of stibethyl surrounded by a frigorific mixture, as long as the colour of the iodine disappears, and leaving the colourless solution to evaporate spontaneously. The iodide then crystallizes in colourless needles, which must be recrystallized from alcohol and afterwards from ether, to free them from a small quantity of a yellow powder which adheres to them.

Iodide of stibethyl has a slight odour of stibethyl and a bitter taste; melts and solidifies at 70·5°; sublimes in small quantity at 100°, without alteration, but is decomposed at a somewhat higher temperature, with formation of dense white fumes. In the fused state, it is instantly decomposed by potassium, with separation of stibethyl. With oil of vitriol and with metallic salts, it behaves like iodide of potassium. Hydro-

loric acid immediately precipitates chloride of stibethyl. Bromine d chlorine separate the iodine; so likewise does nitric acid, with forma- on of nitrate of stibethyl. The iodide dissolves in water without ecomposition, and readily in alcohol and ether.

				Löwig & Schweizer.
12 C	72	15·38		14·92
15 H	15	3·20		3·26
Sb	129	27·57		
2 I	252	53·85		53·98
$(C^4H^5)^3SbI^2$	468	100·00		

Bromide. — Stibethyl takes fire when added in drops to bromine. The bromide is prepared by adding a recently prepared alcoholic solution of bromine to an alcoholic solution of stibethyl cooled by ice, as long as the colour of the bromine disappears. On mixing the solution with a large quantity of water, the bromide of stibethyl is precipitated in the form of a colourless liquid, which must then be washed with water and dried by contact with chloride of calcium.

Transparent, colourless, strongly refracting liquid, having a density of 1·953 at 17°. Has an unpleasant odour like that of turpentine, and excites sneezing. Solidifies in a crystalline mass at −10°. It is not volatile. When distilled, it yields, among other products, a strongly acid liquid having an intolerable odour like that of chloral. It is decomposed by oil of vitriol, with evolution of hydrobromic acid, and by chlorine with separation of bromine. Insoluble in water, but dissolves readily in alcohol and ether. The alcoholic solution gives with metallic salts reactions similar to those of bromide of potassium.

				Löwig & Schweizer.
12 C	72	19·15		18·95
15 H	15	4·00		4·20
Sb	129	34·30		
2 Br	160	42·55		42·53
$(C^4H^5)^3SbBr^2$	376	100·00		

Chloride. — Stibethyl dropt into chlorine gas takes fire and burns with a bright but smoky flame. Introduced into dry hydrochloric acid gas, it forms chloride of stibethyl, and separates a quantity of hydrogen equal in volume to half the hydrochloric acid gas (p. 80). The chloride is also formed, with evolution of hydrogen, by the action of fuming hydrochloric acid on stibethyl. — *Preparation.* The chloride is easily obtained in the pure state by decomposing a strong solution of nitrate of stibethyl with strong hydrochloric acid; it then separates in the form of a liquid which may be purified in the same manner as the bromide.

Transparent, colourless liquid, of sp. gr. 1·540 at 17°; has a powerful odour like that of turpentine, and a bitter taste. Remains fluid at −12°. When it is distilled with water, a small portion appears to volatilize undecomposed; when heated alone it behaves like the bromide. Strong sulphuric acid decomposes it, with evolution of hydrochloric acid; while, on the other hand, hydrochloric acid added to a solution of sulphate of stibethyl, throws down the chloride. In other respects, its reactions are like those of chloride of potassium or chloride of sodium. *It is insoluble in water, but* dissolves readily in alcohol and ether.

				Löwig & Schweizer.		
12 C	72·0	25·11		25·11	25·04	25·11
15 H	15·0	5·22		5·55	5·48	5·41
Sb	129·0	44·98				
2 Cl	70·8	24·69		24·63	24·28	24·20
$(C^4H^5)^3SbCl^2$	286·8	100·00				

Nitrate. — Obtained by saturating dilute nitric acid with oxide of stibethyl, or by dissolving stibethyl in the dilute acid with the aid of a gentle heat. (In this latter reaction, nitric oxide is evolved, and a small quantity of antimonic oxide separates out.) — On evaporating the solution, the salt is obtained in crystals; or, if the acid solution be strongly concentrated over the water-bath, the salt separates in heavy oily drops which solidify in the crystalline form on cooling. By dissolving the salt in a small quantity of water, and leaving the solution to spontaneous evaporation, it is obtained in large rhomboidal crystals melting at 62·5°, into a transparent liquid, which at 57° solidifies in a crystalline mass. The salt when more strongly heated, deflagrates like a mixture of nitre and charcoal. It dissolves readily in water, less easily in alcohol, and is nearly insoluble in ether. The solutions have an acid reaction and bitter taste.

			Löwig & Schweizer.	
12 C	72	21·18	22·26	21·60
15 H	15	4·41	4·55	4·62
Sb	129	37·94		
2 O	16	4·71		
2 NO^5	108	31·76	32·20	
$(C^4H^5)^3SbO^2,2NO^5$	340	100·00		

Antimonite. — Formed, together with the oxide, by the gradual oxidation of stibethyl (p. 81). The white fumes which stibethyl diffuses in the air before taking fire, consist almost wholly of this compound. It is prepared by leaving an ethereal solution of stibethyl to evaporate spontaneously, and dissolving out the simultaneously formed oxide with a mixture of ether and alcohol; the antimonite then remains in the form of a white, pulverulent, amorphous body. — Has a bitter taste, and dissolves in water and in alcohol. The aqueous solution prepared in the cold is perfectly mobile; but when heated, becomes viscid like starch-paste, and dries up to a friable mass like porcelain; water poured upon this mass dissolves the greater part, but leaves a small residue consisting of antimonic oxide. — Hydrochloric acid added to the alcoholic solution, immediately throws down chloride of stibethyl; the acid liquid separated from the chloride yields with sulphuretted hydrogen a precipitate of kermes; and on mixing it with water, a precipitate of algaroth-powder is obtained. (Löwig.)

			Löwig.		
12 C	72	13·38	12·58	12·67	
15 H	15	2·78	2·70	2·78	
3 Sb	387	71·92	68·33	69·04	69·66
8 O	64	11·92			
$(C^4H^5)^3SbO^2,2SbO^3$	538	100·00			

This compound was formerly regarded by Löwig & Schweizer, as ethylo-stibylic acid, $AeSbO^5$, that is to say, as an acid analogous to antimonic acid, and containing a radical, called *ethylostibyl*, formed of 1 At. ethyl and 1 At. antimony.

Sulphantimonite. — 1. Sulphuretted hydrogen passed through a solution of the antimonite, throws down this compound in the form of a light yellow precipitate having an extremely unpleasant, persistent odour, like that of mercaptan. — 2. The compound is also formed by adding recently precipitated tersulphide of antimony to a solution of sulphide of stibethyl, the latter being in excess, whereupon the brown-red colour of the kermes immediately changes to light yellow. Dried over sulphuric acid it forms a powder of a beautiful light yellow colour, which changes to brown-red at the heat of the water-bath. — When distilled over a spirit-lamp, it yields a liquid distillate having all the properties of sulphide of stibethyl. — Dilute sulphuric acid poured upon it, separates tersulphide of antimony, with evolution of sulphuretted hydrogen, and formation of sulphate of stibethyl:

$$Ae^3SbS^2,2SbS^3 + 2SO^3 + 2HO = Ae^3SbO^2,2SO^3 + 2HS + 2SbS^3.$$

Fuming nitric acid decomposes it, with emission of light and heat. (Löwig.)

				Löwig.
12 C	72	....	11·96	..... 11·68
15 H	15	....	2·49	..... 2·59
3 Sb	387	....	64·28	
8 S	128	....	21·27	..... 20·74
$(C^4H^5)^3SbS^2,2SbS^3$	599	....	100·00	

Cyanide. Ae^3SbCy^2. — 2 At. cyanide of mercury and 1 At. sulphide of stibethyl mixed in the state of aqueous solution, form sulphide of mercury, and a liquid which tastes and smells like hydrocyanic acid, behaves with metallic salts like cyanide of potassium, and probably therefore contains cyanide of stibethyl. But it loses these characters in the course of 24 hours, or more quickly when heated; and if it be then boiled with potash, ammonia is given off in large quantity. — When iodide of stibethyl is added to an alcoholic solution of cyanide of mercury, the mercuric iodide precipitated at first redissolves after a while, and the solution yields a salt, in small, hard, yellow, shining crystals, which dissolve in water and alcohol, and probably consist of a compound of cyanide of stibethyl with iodide of mercury. Dilute hydrochloric acid added to a solution of this salt, throws down iodide of mercury, and forms hydrocyanic acid and chloride of stibethyl. (Löwig & Schweizer.)

Stibethylium. — $(C^4H^5)^4Sb$. Known as yet only in the form of an iodide, which is obtained by adding iodide of ethyl to stibethyl. The iodide crystallizes in long beautiful needles, which are easily soluble in water and alcohol. (Landolt.)

Stibmethylethylium. — $(C^2H^3)^3(C^4H^5)Sb$. Obtained as an iodide by mixing stibmethyl with iodide of ethyl. The iodide closely resembles the iodide of stibmethylium (VII, 326). (Landolt.)

Conjugated Compounds containing Bismuth.

¶ Bismethyl. $(C^4H^4)^3BiH^3=(C^4H^5)^3Bi$.

Löwig & Schweizer (1850). *Ann. Pharm.* 75, 355.
Breed. *Sill. Am. J.* [2], 13, 404; *Ann. Pharm.* 82, 106; abstr. *J. pr. Chem.* 56, 341; *Pharm. Centr.* 1852, 445; *N. Ann. Chim. Phys.* 35, 479; *Jahresber.* 1852, 601.
Dünhaupt, *Chem. Gaz.* 1854, 2, 61.

Bismuthide of Ethyl, Bistriethyl. — Discovered by Löwig & Schweizer; more fully examined by Breed and by Dünhaupt.

Formed by the action of iodide of ethyl on bismuthide of potassium. (Löwig & Schweizer.)

Preparation. Bismuthide of potassium* finely pounded, and without admixture of sand, is introduced into a small flask; iodide of ethyl added in excess; the flask closed, and immediately connected with a long narrow distillation-tube passing into a receiver surrounded with ice: all these manipulations being performed as quickly as possible. In a few minutes, the action begins; the mixture becomes heated; and the excess of iodide of ethyl distils over. Water free from air is then introduced into the flask, which is immediately closed and heated in the water-bath till the mass becomes soft and the iodide of potassium is dissolved. The same operations are repeated with a considerable number of flasks; the disintegrated contents transferred as quickly as possible into a large flask filled with carbonic acid; shaken up several times with a large quantity of ether; the ethereal solution mixed with the de-aerated water; and the ether completely distilled off in the water-bath. The bismethyl remains at the bottom of the water, and is purified by distilling it with water (it cannot be distilled alone, without decomposition), shaking it up with a small quantity of dilute nitric acid to free it from oxide, and drying over chloride of calcium. During all these operations, the air must be carefully excluded. (Breed.) 3 lbs. of bismuthide of potassium and 1 lb. of iodide of ethyl yield 4 or 5 oz. of pure bismethyl. (Dünhaupt.)

Properties. Transparent, very mobile liquid, sometimes colourless, but often slightly tinged with yellow. Has an unpleasant odour like that of stibethyl, and its vapour, when inhaled even in small quantity, produces a very disagreeable burning sensation on the tip of the tongue. (Breed.)

				Breed (*mean*).
12 C	72	24		24·49
15 H	15	5		5·26
Bi	213	71		70·30
$(C^4H^5)^3Bi$	300	100		

* This alloy is prepared by carbonizing at a moderate heat a mixture of 600 pts. of finely pounded bismuth and 180 pts. of tartar (5 pts. of bismuth and 4 pts. of tartar: (Dünhaupt) likewise well pulverized; the crucible is then heated in such a manner as to raise it to a white heat in half-an-hour at the farthest; after which the furnace is closed and left to cool. The alloy of bismuth and potassium is found at the bottom of the crucible in the form of a silver-white, crystalline button. It is very fusible, and often remains soft or even liquid after cooling. (See also IV, 444.)

Decompositions. 1. Bismethyl heated alone in a retort, begins to boil at 50°, giving off a gas free from bismuth, which burns with a clear flame, while metallic bismuth separates out in the retort. If the heat be continued, the thermometer rises above 160°, and continues to rise till a sudden and violent explosion takes place, which shatters the apparatus. (Breed.) Decomposition begins between 32° and 42°, and explosion takes place at 150°. (Dünhaupt.) The dilute ethereal solution is also decomposed when left to evaporate in the air, leaving a white residue of hydrated oxide of bismuth (Dünhaupt). — 2. Bismethyl exposed to the air gives off thick yellow vapours and takes fire with slight explosion, diffusing a dense yellow smoke of bismuth-oxide; this effect is best shown by moistening a piece of filtering paper with the liquid and exposing it to the air. — 3. Fuming nitric acid decomposes bismethyl, with explosion and vivid combustion. — 4. Bismethyl burns in chlorine gas with separation of charcoal, and takes fire in contact with bromine. In general, its reactions resemble those of stibethyl. (Breed.) — 5. Bismethyl added to solutions of metallic salts (*e. g.* to nitrate of silver or corrosive sublimate) does not simply throw down the oxide, but is itself decomposed. — On adding an alcoholic solution of bismethyl to a not too dilute solution of protochloride of mercury, the former being poured slowly and with constant stirring into the latter, a very large precipitate of calomel is immediately obtained, and chloride of bismuth and hydrochloric ether are doubless formed at the same time. But if the process be reversed, and a hot dilute alcholic solution of corrosive sublimate be poured in a thin stream and with constant stirring into a dilute alcoholic solution of bismethyl, to which a few drops of hydrochloric acid have been added to prevent separation of oxide of bismuth, no precipitate is formed at first; but after some time a bulky precipitate appears, which however is again completely dissolved if the liquid be heated. The reaction is terminated when a drop of the liquid no longer produces a white precipitate in a solution of corrosive sublimate; by a little care it may be arranged that neither liquid shall predominate. If the liquid be then heated on the water-bath till it becomes perfectly clear, separated, if necessary, from a small quantity of metallic mercury by decantation, and then left to cool, light, crystalline, silvery, iridescent laminæ separate out and gradually fill the whole fluid. These crystals consist of *Chloride of Hydrargethyl* Hg^2AeCl (p. 93); the solution from which they are deposited contains *Chloride of Bisethyl*, $BiAeCl^2$ (Dünhaupt):

$$4HgCl + BiAe^3 = 2(Hg^2AeCl) + BiAeCl^2.$$

Combinations. Bismethyl combines with *Sulphur, Iodine, Bromine,* &c.; but the compounds are less stable than those of stibethyl. It is quite insoluble in *Water,* sparingly soluble in ether, but dissolves readily in absolute alcohol. (Breed.)

Bismethyl and Sulphur. — The sulphide of bismethyl has not yet been obtained in the separate state. When an alcoholic solution of bismethyl is boiled with flowers of sulphur, sulphide of bismuth separates; if the liquid be filtered whilst boiling, it deposits a small quantity of a yellowish brown powder which appears still to contain organic matter. — An ethereal solution of bismethyl saturated with sulphuretted hydrogen and left in a loosely stoppered bottle, deposits crystals of BiS^3 having the metallic lustre. — Bismethyl which has been long exposed to the air under water, gives with sulphuretted hydrogen, first a yellow and after-

wards a brown precipitate. The yellow precipitate also becomes brown when dried, and has the same composition as the brown, viz. that of a compound of 1 At. sulphide of bismethyl with 2 At. tersulphide of bismuth (Dünhaupt).

	Dry.			Dünhaupt.		
12 C	72	8·53	7·87	8·00	8·00
15 H	15	1·78	1·93	1·84	1·84
3 Bi	629	74·52	74·40	73·70	74·62
8 S	128	15·17	15·20	15·10	15·00
$(C^4H^5)^3BiS^2,2BiS^3$	844	100·00	99·40	99·64	99·46

Bismethyl and Iodine. — When iodine is added to an alcoholic solution of bismethyl, heat is evolved, the colour of the iodine disappears, and iodide of bismethyl is formed. This compound is less stable than iodide of stibethyl; when its alcoholic solution is left to itself for a while, iodide of bismuth separates out. (Breed.) — When iodine is added to an alcoholic solution of bismethyl, till its colour no longer disappears, a number of compounds are formed, some which remain in solution while others separate out as red or yellow precipitates. If an alcoholic solution of iodine be added to an ethero-alcoholic solution of bismethyl, till the colour of the iodine begins to be permanent, and a small quantity of water be then added, an amorphous precipitate, sometimes yellowish, sometimes reddish, is thrown down. If it be then filtered and a tolerably large quantity of iodine added to the filtrate, an amorphous reddish yellow precipitate is again produced. If this be quickly removed by filtration, and the filtrate mixed by constant stirring with a considerable quantity of water, a red precipitate of acicular crystals is immediately produced, which while moist is quickly decomposed by light, and must therefore be dried in the dark; its analysis led to no decided result. (Dünhaupt.)

An iodide having the composition $C^{12}H^{15}Bi^3I^3$ or $(C^4H^5)^3Bi^2I^3 + BiI^3$ [or $(C^4H^5)^3BiI^2 + Bi^2I^3$] is obtained by adding iodine to a tolerably strong alcoholic solution of bismethyl, till its colour no longer disappears, filtering from the precipitate, and adding to the filtrate a large quantity of water at 40°. A small quantity of a ruby-coloured liquid separates; and if the watery liquid be poured off from this, a large quantity of beautiful red needle-shaped crystals are formed as it cools; these must be immediately collected and dried in vacuo. — The same compound is formed when bismethyl is left for a considerable time in contact with dilute nitric acid, and then mixed with iodide of potassium. — Sparingly soluble in water, but dissolves pretty readily in alcohol and ether; the solutions have a pale yellow colour. — The compound heated on platinum foil gives off a strong yellow vapour which takes fire on coming in contact with flame. (Dünhaupt.)

			Dünhaupt.
12 C	72	5·35	4·58 to 4·91
15 H	15	1·11	1·43 to 1·57
3 Bi	629	46·73	46·00 to 46·49
5 I	630	46·81	46·96 to 47·17
$C^{12}H^{15}Bi^3I^5$	1346	100·00	

Another iodine-compound, having the formula $(C^4H^5)^4Bi_2C^4H^5I$, is contained in the above-mentioned ruby-coloured liquid; but it is very instable. (Dünhaupt.)

Bismethyl and Bromine. — Bromide of bismethyl appears to be formed

by adding bromine to an alcoholic solution of bismethyl; the solution deposits bromide of bismuth when evaporated (Breed).

A compound having the formula $C^{24}H^{30}Bi^3Br$ or $BiBr + 2BiAe^3$? is formed when an alcoholic solution of bromine is added to an alcoholic solution of bismethyl till the colour of the bromine no longer disappears. On mixing the liquid with water, a white powder is thrown down, and the liquid becomes acid. The powder when dried contains 68·88 p.c. bismuth and 26·88 bromine. [These quantities do not at all agree with the above formula, which requires 71·23 Bi and 9·05 Br.] — The acid solution treated with sulphuretted hydrogen, yields yellow precipitates which soon turn brown, and have the composition $(C^4H^5)^3BiS^2 + 2BiS^3$ (Dünhaupt).

Nitrate of Bismethyl. — Bismethyl dissolves readily in dilute nitric acid; and the solution when first formed contains nitrate of bismethyl, but when evaporated leaves nothing but nitrate of bismuth. (Breed.)

¶ Bisethyl. $C^4H^4,HBi=C^4H^5,Bi$.

DÜNHAUPT. *Chem. Gaz.* 1854, 261.

For the formation of this compound, see page 87. It combines with oxygen, sulphur, iodine, bromine, &c. in the proportion of 1 At. bisethyl to 2 At. O, S, &c.; but the compounds are very difficult to obtain, in consequence of their great proneness to decomposition. The iodide is the only one that is at all stable; and even that can only be preserved when perfectly dry and in the dark.

Oxide. — $C^4H^5BiO^2$. — A solution of iodide of bisethyl in aqueous alcohol yields when mixed with ammonia, a yellowish white precipitate of the hydrated oxide; potash likewise throws down the same precipitate, but redissolves it in excess. If the precipitate formed by ammonia be immediately collected on a filter, washed several times with absolute alcohol, then pressed and dried in vacuo over oil of vitriol, it appears, when examined under the air-pump, to be an amorphous yellow powder; but as soon as it is brought from the vacuum into the air, it ignites and gives off a dense yellow vapour. — This oxide appears also to be formed by the spontaneous oxidation of bismethyl, that radical being first converted, with elimination of 2At. ethyl, into oxide of bisethyl, and ultimately into hydrated oxide of bismuth, $BiO^3,3HO$.

Sulphide. — Obtained by treating the iodide with sulphuretted hydrogen.

Sulphate. — By treating the iodide with sulphate of silver.

Iodide. — $C^4H^5BiI^2$. — When iodide of potassium is added to the solution of chloride of bisethyl obtained by treating corrosive sublimate with bismethyl (p. 87,) the liquid acquires a yellowish-red colour, without becoming turbid. On adding water till turbidity is produced, then heating the liquid on the water-bath till it becomes perfectly clear, and allowing it to cool gradually, the iodide of bisethyl separates in beautiful, golden-yellow, six-sided laminæ, which must be pressed between blotting paper and dried in vacuo; they then possess a perfect golden

lustre. Scarcely soluble in water, and sparingly in ether, to which it imparts a pale yellow colour; but dissolves pretty readily in alcohol even when hydrated. Stable when kept in the dark and perfectly dry; but if it be left for some time under the mother-liquor, which still contains excess of iodide of potassium, the red crystals disappear, and are converted into small, black, metallic, crystalline granules of iodide of bismuth, BiI^3, the supernatant liquid retaining a strong yellow colour.

			Dünhaupt.
4 C	24	4·87	5·21
5 H	5	1·01	1·35
Bi	213	43·11	41·96 to 42·49
2 I	252	51·01	50·20 „ 51·60
$C^4H^5BiI^2$	494	100·00	

Chloride. — Contained in the alcoholic solution obtained by the action of bisethyl on protochloride of mercury. The solution evaporated on the water-bath to a small residue remains perfectly transparent; but on cooling a small quantity of chloride of hydrargethyl separates, and must be got rid of by filtration. On leaving the filtrate to evaporate spontaneously, crystals are obtained, consisting in all probability of chloride of bisethyl. They do not however dissolve completely in water, but leave a white powder. Iodide of potassium added to the dissolved portion throws down iodide of bisethyl.

Nitrate. — Obtained by adding nitrate of silver to the solution of the iodide. (Dünhaupt.)

¶ Zincethyl or Zincethylium. $C^4H^5Zn = C^4H^4, ZnH = C^4H^5, Zn$.

Frankland. *Phil. Trans.* 1852; *vid.* also *Memoirs* cited on page 91.)

Formed, together with iodide of zinc and free ethyl, when granulated zinc is heated with iodide of ethyl in a sealed tube (VII., 171; VIII., 168, 361):

$$C^4H^5I + 2Zn = ZnI + C^4H^5Zn.$$

On opening the tube, a quantity of gas escapes, after which the zincethyl may be distilled at a gentle heat in an atmosphere of hydrogen, and collected in small glass bulbs terminating in capillary tubes.

Transparent, colourless, strongly refracting liquid, having a peculiar pungent odour.

	Calculation.	
4 C	24·0	39·22
5 H	5·0	8·17
Zn	32·2	52·61
C^4H^5Zn	61·2	100·00

Zinc-ethyl resembles zinc-methyl (VII, 329) in its chemical reactions, but is less energetic. It oxidizes in the air, but does not take fire spontaneously, unless a considerable quantity of it be exposed to the air. In

contact with water, it is immediately resolved into oxide of zinc and hydride of ethyl:

$$C^4H^5Zn + HO = ZnO + C^4H^5,H.$$

When left to oxidize slowly, it forms a white amorphous oxide. Combines also directly with iodine, bromine, and chlorine.

¶ *Conjugated Compounds containing Tin: Stannethyls.*

FRANKLAND. *Phil. Trans.* 1852; *Phil. Mag. J.* [4], 5, 239; *Ann. Pharm.* 85, 329; *J. pr. Chem.* 58, 421; abstr. *Chem. Soc. Qu. J.* 6, 57; *Jahresber.* 1852, 569.

CAHOURS & RICHE. *Compt. rend.* 35, 91; *Instit.* 1852, 229; *Ann. Pharm.* 84, 333; *Jahresber.* 1852, 576.

LÖWIG. *Mittheel. d. naturforsch. Gesellsch. in Zürich*, Oct. 1852; *J. pr. Chem.* 57, 385; *Chem. Gaz.* 1853, 101, 126, 149, 170; abstr. *Ann. Pharm.* 84, 308; *N. Ann. Chim. Phys.* 37, 343; *N. J. Pharm.* 23, 234; *Jahresber.* 1852, 577.

Frankland obtained stannethyl in the form of an iodide, C^4H^5Sn,I, by the action of tin on iodide of ethyl, under the influence of light or heat. The same product has been obtained in a similar manner by Cahours and Riche; and Löwig, by acting upon an alloy of tin and sodium or potassium with iodide of ethyl, has obtained the same radical, together with several others, partly in the free state, partly combined with iodine, viz. :—

	$C^4H^5Sn = AeSn$
Stannethyl	
$\frac{2}{2}$-stannethyl *or* Methylene-stannethyl	Ae^2Sn^2
$\frac{4}{4}$-stannethyl *or* Ethylene-stannethyl	Ae^4Sn^4
$\frac{3}{4}$-stannethyl *or* Aceto-stannethyl	Ae^3Sn^4
$\frac{3}{3}$-stannethyl *or* Methylo-stannethyl	Ae^3Sn^3
$\frac{5}{4}$-stannethyl *or* Ethylo-stannethyl	Ae^5Sn^4
$\frac{6}{6}$-stannethyl	Ae^6Sn^6

Löwig regards these compounds as analogous to hydrocarbons.

For the simultaneous formation of the radicals and their iodides, Löwig suggests the two following explanations: (1.) Iodide of ethyl and stannide of sodium first form stannethyl and iodide of sodium (Löwig ascertained that no iodide of tin is formed); the stannethyl then acts upon another portion of iodide of ethyl, forming iodide of stannethyl; and the ethyl thus set free combines with the excess of tin, reproducing stannethyl. Whether the iodide of stannethyl is reduced or not and the stannethyl contained in it set free, depends upon the greater or smaller quantity of sodium present. — (2.) The reaction takes place between 2 At. iodide of ethyl, 2 At. tin, and 1 At. sodium.

$$2C^4H^5I + 2Sn + Na = C^4H^5Sn + C^4H^5SnI + NaI,$$

the iodide of stannethyl being wholly or partially reduced according to the excess of sodium present. Other proportions between the quantities of the acting substances give rise to the formation of the other stannethyls and their iodides.

Phosphide of tin and iodide of ethyl yield iodide of stannethyl, iodide of methylene-stannethyl, $(C^4H^5)^2Sn^2I$, and one of the liquid iodides obtained by Löwig (p. 94).

Preparation, according to Löwig. — Stannide of sodium prepared by fusing 6 parts of tin with 1 pt. of sodium* is finely pulverized, and mixed with quartz-sand in the proportion of 1 pt. of the alloy to 1....1½ pts. of sand; the mixture quickly introduced into a number of glass flasks of 3 or 4 ounces capacity; and a quantity of iodide of ethyl added, sufficient to form a thick paste: the flask is then briskly shaken, and a distillation-tube adapted to it. The action commences in a few minutes, and is completed the more quickly in proportion as the alloy is richer in sodium. The heat which it develops is sufficient to cause the excess of iodide of ethyl to distil over, after which, the flask while yet warm is closed air-tight; after the mixture has cooled, the treatment with iodide of ethyl is renewed, and the same operations repeated till a sample of the contents of the flask no longer gives off hydrogen when thrown into water. The dry, dusty, yellowish, stinking mass obtained in this manner from several flasks, is then transferred to a bottle filled with ether (from 4½ to 5 pounds to the contents of 16 flasks), left to stand for an hour or two, and frequently shaken; after which, the dark brown ethereal solution is poured into a bottle filled with carbonic acid, and left to stand for half an hour or an hour, whereupon, especially if there were any air in the bottle, a brown substance, which dries up in the air to a white inodorous mass, separates out. The ethereal solution contains five or six organic radicals and a number of iodine-compounds, the quantity of the latter being greatest when the flask does not contain any undecomposed iodide of sodium.

General Properties of the Stannethyls. — These compounds are at ordinary temperatures, viscid liquids, like turpentine or palm-oil. They have a faint odour like that of rotten fruit, and when rubbed between the fingers, impart a strong smell of tin; their taste is disagreeably sharp and burning. They are insoluble in water and exhibit no adhesion to it; insoluble or sparingly soluble in alcohol, but dissolve readily in ether; their iodides are readily soluble in alcohol, even when hydrated. The stannethyls do not take fire spontaneously, or even fume when exposed to the air; when set on fire, they burn with a very bright flame, emitting sparks and diffusing a thick white vapour of stannic oxide. When the ethereal solution of these radicals is left to evaporate in the air, they oxidize, some of them being converted into white amorphous powders, others into syrupy liquids which crystallize after a while. The former oxides are nearly inodorous; insoluble in water, alcohol, and ether; form crystallizable salts; and are precipitated from their solutions by ammonia; — the latter have a very powerful odour like that of oil of mustard; dissolve sparingly in water, but readily in alcohol and ether; form liquid haloïd compounds; have very strong basic properties; and separate ammonia from its salts. — All the stannethyls take fire and

* To prepare this alloy, 6 pts. of tin are fused in an earthen crucible, 1 pt. of sodium still moistened with rock-oil added by small portions, and the mixture well stirred with an iron rod. The small quantity of naphtha adhering to the sodium, takes fire, and the gases produced by the combustion prevent the access of air to the mixture. The mixture when cooled forms a silver-white, crystalline alloy, easier to pulverize and less oxidable than the corresponding alloy of potassium; it must be preserved in a stoppered bottle filled up with quartz-sand. — The alloy obtained by fusing 3 or 4 pts. of tin with 1 pt. of sodium dilates considerably in solidifying, often breaking the crucible. The former alloy is by far the more convenient for preparing the stannides of ethyl.

explode on the addition of a few drops of fuming nitric acid; with dilute nitric acid, they give off nitric oxide, and are converted into nitrates. They exhibit generally the character of electro-positive metals, uniting readily with iodine, bromine, chlorine, &c.; the union with bromine and chlorine is attended with momentary combustion. With hydracids, *e. g.*, with hydrochloric acid, they evolve hydrogen and form haloïd salts. — The ethereal solution of the stannethyls added to an alcoholic solution of nitrate of silver, immediately throws down metallic silver in the form of a black powder; the iodides form a yellow precipitate of iodide of silver. (Löwig.)

Separation of the individual radicals. — *a.* The ethereal solution was mixed with $\frac{1}{12}$ to $\frac{1}{10}$ of absolute alcohol and the liquid distilled over the water-bath. After all the ether had passed over, there remained in the retort a dark red, nearly black mass (A), of the consistence of turpentine, which was a mixture of several stannides of ethyl. The hot alcoholic solution decanted into a vessel filled with carbonic acid deposited after 24 hours, a yellow oil (B). — To the alcoholic mother-liquor from which this oil had been deposited, water was added drop by drop, till a sample of the liquid no longer reduced an alcoholic solution of nitrate of silver, but threw down a precipitate of pure iodide of silver; a colourless oil (C) was then deposited. — The remaining alcoholic liquid (D) contained nothing but the iodides of the stannethyls.

The mass A dissolved but sparingly in alcohol, even at a boiling heat, and separated out again completely on cooling. The dark red ethereal solution became colourless on the addition of a small quantity of alcohol, and deposited a black greasy mass, probably containing the radical $(C^4H^5)^4Sn^6$. — The decolorized ethereal solution evaporated out of contact of air, left a nearly colourless viscid liquid of sp. gr. 1·654, which dissolved readily in ether, and was gradually but not completely precipitated by alcohol. The compound thus precipitated was *Stannethyl*, C^4H^5Sn.

The yellow oil B separated after a while into two layers, the lower of which consisted chiefly of stannethyl. The upper, greenish yellow, viscid stratum was dissolved in ether and shaken up with strong potash, whereupon a thick black mass separated, containing stannethyl and *Acetostannethyl* $(C^4H^5)^3Sn^4$. The ethereal solution still contained the same two radicals, which, after the ether was evaporated, remained in the form of a colourless, oily liquid. On converting these radicals into iodides, dissolving the iodides in alcohol, and leaving the solution to evaporate, the iodide of acetostannethyl crystallized out first, and then the iodide of stannethyl.

The different portions of the liquid C were more fluid and volatile, the later they were separated out during the gradual addition of water. The first portions consisted chiefly of stannethyl; the latter portions yielded syrupy iodides having a very offensive odour, and these, after standing for some time, yielded rhombic crystals of iodide of *Ethylene-stannethyl* $(C^4H^5)^4Sn^4$. — The syrupy liquid separated from the crystals contained several volatile iodine-compounds, which could not be completely separated by fractional distillation with water. The first and more volatile portion of the distillate was decomposed with recently precipitated oxide of silver; and the strongly alkaline alcoholic liquid filtered from the iodide of silver, left, when evaporated, a few mammellated and a large number of prismatic crystals, consisting of the hydrated

oxides, the former of *Ethylostannethyl* $(C^4H^5)^5Sn^4$, the latter of *Methylostannethyl* $(C^4H^5)^3Sn^2$. The more viscid portion of the distillate which afterwards passed over, yielded by similar treatment a small number of the prismatic and a large number of the mammellated crystals. The separation of the two radicals is rendered more complete by converting them into sulphates, the sulphate of ethylostannethyl being less soluble in alcohol than the sulphate of methylostannethyl.

The solution D contained the iodides of the radicals, in quantity varying according to the composition of the stannide of sodium, and the relative quantities of the alloy and of iodide of ethyl used in the preparation. An alloy of 1 pt. of sodium to 6 pts. of tin, mixed with an equal weight of quartz-sand, and added in excess, yielded no iodides, but only the free radicals; but when alloys were used containing a larger proportion of sodium, and the iodide of ethyl was added in excess, iodides of the radicals were always formed. Some of these compounds were crystallizable, and after exposure to the air for some time, inodorous; others were liquid, generally oily, and had a powerful odour. The former were sometimes formed in such quantity, that they partly separated in the crystalline form, together with the radicals, from the ethero-alcoholic solution (p. 93); after the distillation of the ether, they may be separated from the radicals by their solubility in cold alcohol. Generally, however, they remained in solution, and were then found in the alcoholic liquid D, from which the radicals had been precipitated by the gradual addition of water. This liquid, abandoned to spontaneous evaporation, frequently yielded at first small hard crystals, sparingly soluble in alcohol, and separating in tables from the hot alcoholic solution: these consisted of iodide of *Methylene-stannethyl*, $(C^4H^5)^3Sn^2I$; afterwards a considerable number of needle-shaped crystals of iodide of aceto-stannethyl generally separated in stellate groupes; and after complete evaporation, there remained a fluid mass, sometimes comparatively thin, sometimes viscid. On dissolving this liquid mass in alcohol, agitating the solution with ether and a sufficient quantity of water to separate the ether, and evaporating the ethereal solution, rhombic tables of iodide of ethylene-stannethyl separated from the residue, whilst iodide of methylostannethyl and iodide of ethylostannethyl remained in the oily liquid; the diluted alcohol likewise retained iodide of stannethyl in solution. (Löwig.)

b. When it is desired to obtain, not the radicals themselves, but certain of their compounds, the following methods of separation are preferable to the one just given.

1. To the ethereal solution of the products obtained by the action of iodide of ethyl on stannide of sodium (p. 92), iodine is added as long as it is dissolved and its colour destroyed, after which the liquid is mixed with alcohol, and the ether completely distilled off. The iodides are converted into oxides by mixing the alcoholic solution with recently precipitated oxide of silver previously washed with alcohol. The resulting oxides of methylostannethyl and ethylostannethyl are soluble in alcohol; those of the other radicals are insoluble, and go down with the iodide of silver. After filtering and washing with alcohol, the alcoholic, strongly alkaline liquid is exactly neutralized with sulphuric acid previously diluted with alcohol; the sulphates of methylostannethyl and ethylostannethyl, which crystallize out by spontaneous evaporation, are separated by recrystallization; the pure salts redissolved in alcohol, and

decomposed with an exactly equivalent quantity of baryta-water; and the solutions of the pure oxides used for the preparation of the other salts. — The residue on the filter (consisting of iodide of silver, excess of oxide of silver, and insoluble oxides of radicals), is mixed with alcohol to the consistence of a thin paste; strong hydrochloric acid mixed with alcohol gradually added till slightly in excess; and the alcoholic solution of the chlorides of the radicals separated from chloride and iodide of silver, which is best effected by pressure between fine linen. This solution, when left to evaporate, deposits successively the chlorides of methylene-stannethyl, acetostannethyl and ethylene-stannethyl, from which the pure oxides may be precipitated by ammonia (not by potash). — Or, the alcoholic solution of all the iodides is mixed with strong ammonia, which throws down all the oxides excepting those of methylo-stannethyl and ethylo-stannethyl; the white precipitate collected on a filter, washed with alcohol, and dissolved in hydrochloric or some other acid (which must, however, be mixed with alcohol); and the individual salts obtained by fractional crystallization. The alcoholic filtrate still contains the iodides of methylo-stannethyl and ethylo-stannethyl: on mixing it with water and agitating with ether, the ether takes up the iodides, which must then be treated with oxide of silver as above.

2. The ethereal solution of the radicals and their iodides is mixed with alcohol till the radicals begin to separate out, after which an alcoholic solution of nitrate of silver is added, care being taken to avoid an excess. Before filtering, the liquid is placed in a moderately warm situation till the ether is completely volatilized, whereupon the nitrates of certain radicals, which are insoluble or only sparingly soluble in alcoholic ether, redissolve. The liquid is then filtered; the filtrate slowly evaporated to dryness over the water-bath; and the residue treated with ether, which leaves undissolved some small white crystals; and on dissolving these crystals in hydrated alcohol and slowly evaporating the solution, crystals of nitrate of acetostannethyl are first obtained, and afterwards crystals of nitrate of stannethyl. The ethereal solution yields by evaporation a crystalline mass and an oily liquid, which becomes opaque and solid on cooling. The crystalline mass is a mixture of nitrate of ethylene-stannethyl, nitrate of acetostannethyl, and a small quantity of nitrate of stannethyl. The varnish-like residue consists of nitrate of methylostannethyl and nitrate of ethylostannethyl; on dissolving it in absolute alcohol and digesting with carbonate of baryta, the bases remain dissolved in the alcohol, and may be obtained in crystals by evaporation.

3. The ethereal solution of the radicals and iodides is mixed with alcohol, and the mixture left to evaporate in a wide glass vessel. A slow oxidation of the radicals then takes place; and the oxides which are insoluble in alcohol, separate out as a white powder, while the iodides and the oxides of methylostannethyl and ethylostannethyl remain dissolved in the alcohol. The separated oxides are then dissolved in alcoholic hydrochloric acid, and the resulting chlorides separated by crystallization. The separation of the iodides and of the oxides of methylostannethyl and ethylostannethyl is effected in the manner already described. (Löwig.)

¶ Stannethyl or Stannethylium. $C^4H^5Sn = C^4H^4SnH = C^4H^5,Sn$.

Preparation. 1. By the action of zinc on a salt of stannethyl. A strip of zinc immersed in a solution of chloride of stannethyl, soon becomes covered with dense yellow oily drops, which finally separate from the lower extremity of the zinc, and accumulate at the bottom of the vessel. The formation of the oily liquid is much favoured by a gentle heat. It is purified by washing with water, and drying over chloride of calcium. (Frankland.) — 2. Stannethyl is also found in the free state, among the products of the action of iodide of ethyl on stannide of sodium. (Löwig, pp. 91–95.)

Properties. Thick, heavy, oily liquid, probably colourless when pure, but generally exhibiting a yellow or brownish yellow colour. (Frankland, Löwig.) Has a very pungent odour, resembling that of its compounds, but much more powerful. (Frankland.) Sp. gr. 1·558 at 15°. (Löwig.) Does not solidify at —12°. (Löwig.) Begins to boil at 150°, depositing metallic tin, and yielding a colourless distillate which has a peculiar odour, and probably consists of $(C^4H^5)^2Sn$. (Frankland.) Insoluble in water, soluble in alcohol and ether. (Frankland.) Sparingly soluble in alcohol, readily in ether. (Löwig.)

			Frankland.	Löwig.
4 C	24	27·27	26·95	27·00 to 28·07
5 H	5	5·68	5·51	5·83 ,, 6·00
Sn	59	67·05		66·89
C^4H^5Sn	88	100·00		

Oxide. — Stannethyl exposed to the air, either in the free state or dissolved in ether, rapidly absorbs oxygen, and is converted into a white pulverulent oxide. (Löwig). The oxide is also precipitated by ammonia from solutions of the salts. (Frankland, Löwig.)

Cream-white amorphous powder, closely resembling stannic oxide, but not so heavy; has a peculiar slightly ethereal odour and a bitter taste. (Frankland.) White, non-volatile powder, destitute of taste and smell. (Löwig.)

			Frankland.	Löwig.
4 C	24	25·00	25·09	25·09
5 H	5	5·21	5·18	5·47
Sn	59	61·46	61·99	
O	8	8·33		
C^4H^5SnO	96	100·00		

Oxide of stannethyl heated in the air, takes fire and burns with a bright flame, giving off dense fumes of stannic oxide. It is insoluble in water, alcohol, and ether, but dissolves readily in acids, forming crystallizable salts. (Frankland.) According to Löwig, they crystallize with difficulty. — The reactions of these salts closely resemble those of the stannic salts. Ammonia precipitates the oxide permanently; potash also precipitates it, but redissolves it in excess. (Frankland, Löwig, Cahours, and Riche.) All the salts are inodorous, soluble in water and

alcohol, and sparingly in ether. (Löwig.) Those which contain strong acids exhibit an acid reaction.

Sulphide. C^4H^5SnS. — Formed by passing sulphuretted hydrogen through a solution of a stannethylic salt:

$$AeSnO + HS = AeSnS + HO.$$

White precipitate, insoluble in dilute acids and in ammonia, but soluble in strong hydrochloric acid and in solutions of the fixed alkalis and alkaline sulphides. Has a very pungent and repulsive odour like that of decaying horse-radish. When heated, it melts, froths up, and decomposes, giving off vapours which have a most insupportable odour. Heated with nitric acid, it is decomposed and stannic oxide formed. (Frankland.)

The *Carbonate* and *Phosphate* of stannethyl are insoluble in water. (Cahours & Riche.)

Sulphate. Obtained by decomposing the iodide with sulphate of silver. Crystallizable, soluble in water and alcohol. (Löwig.) Crystallizes in small nacreous scales. (Cahours & Riche.)

				Löwig.
4 C	24	17·64		17·20
5 H	5	3·67		3·90
Sn	59	43·40		
O	8	5·88		
SO^3	40	29·41		28·78
C^4H^5SnO,SO^3	136	100·00		

Iodide. — 1. Formed by adding iodine to an ethereal solution of stannethyl as long as its colour is destroyed, and leaving the solution to evaporate. (Löwig.) — 2. By the action of tin on iodide of ethyl. When iodide of ethyl and metallic tin are placed together in sealed tubes, and exposed to the action of heat or to the direct rays of the sun, the tin gradually dissolves, and the liquid is ultimately converted into a mass of nearly colourless crystals. The reaction is most conveniently effected by the influence of light, an excess of tin cut into narrow strips being employed. The sealed tubes containing the ingredients, should be placed near the focus of a large parabolic reflector, the temperature being prevented, if necessary, from rising too high, by immersing the tubes in water, or in a solution of sulphate of copper. The unconcentrated rays of the sun, or even diffused daylight, are quite sufficient to determine the formation of the crystalline body; but an exposure of several weeks, or even months, would be necessary for the completion of the change which, by the use of the reflector, is effected in a few days of bright sunshine. The liquid gradually assumes a straw-yellow colour; but its solidification must be prevented as long as possible towards the close of operation, by allowing the temperature to rise to 35° or 40°: nearly all the iodide of ethyl then enters into combination with the tin. When heat instead of light is employed to effect the combination, the tubes should not be more than half an inch in diameter, and to avoid risk of explosion, should be only one-fourth filled with the materials; combination then takes place at about 180°. The product is the same, whether heat or light be employed; but the agency of light is the more conve-

nient of the two. The crystalline product, which consists of iodide of stannethyl, is dissolved in boiling alcohol, and the solution evaporated in vacuo. — This reaction is always attended with the production of a small quantity of gas, consisting of olefiant gas and iodide of ethyl, proceeding from a secondary action. (Vid. VIII, 361.) (Frankland.) — Cahours & Riche likewise prepare the iodide of stannethyl by heating iodide of ethyl with tin-foil in a sealed tube to a temperature between 160° and 180°, and extracting with alcohol.

Crystallizes in transparent, slightly straw-coloured needles, which have the form of right rectangular prisms, often $\frac{1}{12}$ of an inch broad and 2 or 3 inches long (Frankland). — Beautiful colourless needles, often 4 inches long (Löwig). Long shining needles, having a slight yellowish tint when partially decomposed, as by exposure to sunshine, but becoming colourless after pressure between bibulous paper. (Cahours & Riche.) Has a peculiar pungent odour, somewhat like that of oil of mustard, and irritates the eyes and lining membrane of the nose, causing a discharge which continues for several hours or even days, especially if the vapour from the heated compound be inhaled. (Frankland.) Nearly inodorous when pure, but before purification, has a strong odour like that of turnips. (Cahours & Riche.) Melts at 38° (Cah. & Riche); at 42° (Frankland) forming a colourless oil. Not perceptibly volatile at ordinary temperatures, inasmuch as a few grains may be exposed to the air for several weeks without loss of weight. (Frankland.) When slowly heated above its melting point, it sublimes in beautiful, long, colourless needles. (Löwig; Cahours & Riche.) Boils at 240°, with partial decomposition. (Frankland.) Dissolves sparingly in cold water and alcohol (Frankland; Cahours & Riche); but when heated with water, it is converted into a colourless oil which sinks in the water and gradually dissolves. (Cahours & Riche.) The aqueous solution is decomposed by boiling, oxide of stannethyl being precipitated and hydriodic acid formed. (Frankland.) Dissolves readily in boiling alcohol, and still more in ether. (Frankland; Cahours & Riche.) The solution behaves with salts of lead, silver, mercury, &c. just like iodide of potassium. (Cahours & Riche.)

				Frankland.	Löwig.	Cah. & Riche.
4 C	24	11·22		11·19	11·18	11·06
5 H	5	2·33		2·33	2·34	2·48
Sn	59	27·57		27·12		
I	126	58·88		58·76	58·89	58·22
C^4H^5SnI	214	100·00		99·40		

Bromide. — Prepared like the iodide (Löwig); by mixing the alcoholic solutions of stannethyl and bromine. (Frankland.) Crystallizes by spontaneous evaporation in long white needles resembling the iodide in appearance and in chemical reactions (Löwig, Frankland):

			Frankland.	Löwig.
4 C	24	14·28	14·32	14·08
5 H	5	3·00	2·95	3·12
Sn	59	35·12		
Br	80	47·60		47·36
C^4H^5SnBr	168	100·00		

Chloride. Prepared by dissolving oxide of stannethyl in dilute hydrochloric acid. On evaporating at a gentle heat (Frankland), or by spon-

taneous evaporation (Löwig), the chloride crystallizes in long colourless needles, isomorphous with the iodide. Melts somewhat above 30°, and when quickly cooled, solidifies in an amorphous mass. (Löwig.) More volatile and more pungent than the iodide. (Frankland.) Very volatile, and sublimes below its melting point in fine hard crystalline needles. (Löwig.) In its chemical relations it resembles the iodide and bromide.

				Löwig.
4 C	24·0	19·43		18·70 to 18·80
5 H	5·0	4·05		4·80 „ 4·00
Sn	59·0	47·78		
Cl	35·4	28·74		28·30 „ 28·25
C^4H^5SnCl	123·4	100·00		

Nitrate. Obtained by dissolving the oxide in dilute nitric acid (Löwig), or by decomposing the iodide with nitrate of silver. (Löwig; Cahours & Riche.) Forms tolerably large crystals, which melt when heated and burn away with slight detonation (Löwig):

			Löwig.
4 C	24	16·00	15·66
5 H	5	3·33	3·13
Sn	59	39·34	
O	8	5·33	
NO^5	54	36·00	34·93
C^4H^5SnO,NO^5	150	100·00	

The *Formiate* and *Acetate* of stannethyl are soluble in water and crystallizable. (Cahours & Riche.)

Stannmethyl is formed by the action of tin on iodide of methyl, assisted by light or heat. Its compounds resemble those of stannethyl. (Frankland, Cahours & Riche.)

¶ Methylene-stannethyl. $(C^4H^5)^2Sn^2$.

This compound is polymeric with stannethyl. It does not occur in the free state among the radicals produced by the action of iodide of ethyl on stannide of sodium, but was obtained as an iodide in the manner already described (p. 94).

Oxide. $(C^4H^5)^2Sn^2O$.—Precipitated from the solutions of its salts by ammonia. Resembles oxide of stannethyl.

Iodide. — *Preparation* (p. 94). Cahours & Riche have likewise obtained this compound, together with iodide of stannethyl, by the action of tin on iodide of ethyl; also by the action of phosphide of tin on iodide of ethyl. (*Ann. Pharm.* 88, 318.)

			Löwig.
8 C	48	15·90	15·13 14·84
10 H	10	3·31	3·32 3·12
2 Sn	118	39·07	
I	126	41·72	41·25
$(C^4H^5)^2Sn^2I$	302	100·00	

Chloride. Obtained by dissolving the oxide in hydrochloric acid. Sparingly soluble in alcohol. Crystallizes from the hot alcoholic solution in shining white laminæ. (Löwig.)

					Löwig.
8 C	48·0	....	22·71	.....	21·24
10 H	10·0	....	4·73	.....	4·96
2 Sn	118·0	....	55·82		
Cl	35·4	....	16·74	.....	16·95
$(C^4H^5)^2Sn^2Cl$	211·4	....	100·00		

¶ Ethylene-stannethyl or Elayl-stannethyl. $(C^4H^5)^4Sn^4$.

Also polymeric with stannethyl. Found among the radicals which are precipitated by water from the cold alcoholic solution, after the greater part of the stannethyl and acetostannethyl have separated out. (p. 93.) By fractional precipitation, a portion may be obtained consisting chiefly of ethylene-stannethyl, perfectly colourless, oily, and of sp. gr. 1·410.

Oxide. — $(C^4H^5)^4Sn^4O$. — Snow-white, amorphous powder, resembling oxide of stannethyl; perfectly insoluble in water, sparingly soluble in boiling alcohol; more abundantly in ether, but separates from the solution in the form of an amorphous powder. With acids it forms colourless salts, which are soluble in alcohol and ether, but are precipitated from their alcoholic solutions by a large quantity of water, a property which distinguishes them from the salts of stannethyl. Ammonia throws down the oxide as a permanent flocculent precipitate; potash also precipitates it, but redissolves it in excess. The salts in the dry state are greasy to the touch like camphor, and have a faint but peculiar odour.

Iodide. *Preparation,* (pp. 93, 94). Generally crystallizes in rhombic tables, but frequently also in scaly and acicular crystals; unctuous to the touch and very friable. Perfectly insoluble in water, but easily soluble in alcohol and ether.

					Löwig.
16 C	96	....	20·08	.....	19·14 to 19·71
20 H	20	....	4·18	.....	4·22 „ 4·52
4 Sn	236	....	49·38	.....	49·22
I	126	....	26·36	.....	25·10 to 26·51
$(C^4H^5)^4Sn^4I$	478	....	100·00		

Bromide. — Obtained by saturating with bromine the mixture of radicals precipitated by water from the ethero-alcoholic solution (p. 93) and leaving the solution to evaporate; the crystals which form in the oily residue must be pressed and recrystallized from ether; the last portions which separate out consist of bromide of ethylene-stannethyl, which may be purified by repeated crystallization from ether (Löwig):

					Löwig.		
16 C	96	....	22·22	.....	21·40	.... 22·22	.... 22·17
20 H	20	....	4·63	.....	4·56	.... 4·78	....
4 Sn	236	....	54·63				
Br	80	....	18·52	.....		18·08	
$(C^4H^5)^4Sn^4Br$	432	....	100·00				

Chloride. — Crystallizes out last when the solution of the mixed oxides (p. 95) in alcoholic hydrochloric acid is left to evaporate. Resembles the preceding compounds.

Nitrate. — Obtained by dissolving the last portions of the mixed radicals precipitated by water from the cold alcoholic solution (p. 93) in a mixture of alcohol and ether; mixing the dissolved radicals with a quantity of nitrate of silver exactly sufficient for their transformation; filtering the liquid from the silver-precipitate; and evaporating at a gentle heat. The oily residue, after a while, yields crystals which are only partially soluble in ether. The dissolved portion consists of nitrate of ethylene-stannethyl which crystallizes out from the ethereal solution; but it is only the last portions that consist of the pure compound. (Löwig.)

			Löwig.
16 C	96	23·14	22·23
20 H	20	4·83	5·02
4 Sn	236	57·01	
O	8	1·98	
NO^5	54	13·04	13·43
$(C^4H^5)^4Sn^4O,NO^5$	404	100·00	

¶ Acetostannethyl. $C^{12}H^{15}Sn^4=(C^4H^5)^3Sn^4$.

Separates from the alcoholic solution of the radicals (p. 93) after it has been freed from ether and cooled. It likewise constitutes the first portion of the mixture of radicals precipitated on adding water to the cold alcoholic solution. It has not been obtained quite pure.

	Calculation.	
12 C	72	22·29
15 H	15	4·64
4 Sn	236	73·07
$(C^4H^5)^3Sn^4$	323	100·00

Oxide. — Precipitated from the iodide by ammonia as a white amorphous powder, soluble in aqueous potash. In its chemical relations, it stands next to the oxide of ethylene-stannethyl. Its salts are scarcely soluble in water, but dissolve in alcohol. The nitrate is also soluble in ether.

Iodide. — *Preparation* (pp. 93, 94). Crystallizes from the ethereal solution, generally in beautiful needles arranged in stellate groups, but frequently also, especially from the alchoholic solution, in small needle-shaped crystals. It is insoluble in water, but dissolves readily in alcohol and ether, less easily however than iodide of ethylene-stannethyl. Nearly inodorous.

			Löwig.
12 C	72	16·04	15·25 to 15·50
15 H	15	3·34	3·41 ,, 3·60
4 Sn	236	52·56	51·64
I	126	28·06	28·06 to 28·78
$(C^4H^5)^3Sn^4I$	449	100·00	

Bromide. — Obtained by saturating with bromine the ethereal solution of the mixture of radicals precipitated by water from the cold alcoholic solution (p. 93), and leaving it to evaporate spontaneously; the bromide then separates out first in small needle-shaped crystals:

				Löwig.
12 C	72	....	17·87	
15 H	15	....	3·72	
4 Sn	236	....	58·56	
Br	80	....	19·85	20·50
$(C^4H^5)^3Sn^4Br$	403	....	100·00	

Nitrate. — Obtained, together with nitrate of ethylene-stannethyl, by treating the mixture of the radicals precipitated by water from the cold alcoholic solution (p. 93), with nitrate of silver, whereby they are converted into nitrates. As it is but sparingly soluble in ether, it may be obtained tolerably pure by repeatedly treating the mixture of the nitrates with cold ether and recrystallizing from the ethero-alcoholic solution. (See also page 95.) But to obtain a perfectly pure salt, it is necessary to decompose the pure iodide with an exactly equivalent quantity of nitrate of silver dissolved in alcohol. — Crystallizes in small, shining, tolerably hard crystals, which burn away without detonation when heated. (Löwig.)

				Löwig.
12 C	72	....	18·70	18·32
15 H	15	....	3·89	4·67
4 Sn	236	....	61·30	
O	8	....	2·09	
NO^5	54	....	14·02	13·67
$(C^4H^5)^3Sn^4O,NO^5$	385	....	100·00	

¶ Methylostannethyl. $(C^4H^5)^3Sn^2$.

This compound and ethylostannethyl form the principal part of the last portions precipitated by water from the cold alcoholic solution of the radicals, and are distinguished from the preceding portions by their greater volatility.

	Calculation.		
12 C	72	.....	35·12
15 H	15	.....	7·32
2 Sn	118	.....	57·56
$(C^4H^5)^3Sn^2$	205	.....	100·00

Oxide. $(C^4H^5)Sn^2O$. — Obtained by treating the alcoholic solution of the pure sulphate (prepared as described on page 93), with baryta-water; evaporating the whole to dryness at 80°; agitating the residue with absolute alcohol; and evaporating the filtrate under a bell-jar with sulphuric acid. When the liquid has attained a certain degree of concentration, beautiful, transparent, prismatic crystals are formed, consisting of the hydrated oxide, probably containing water of crystallization. (See also p. 94.)

The crystals melt below 100° to an oily liquid, and volatilize very

gradually. If they be melted over the water-bath, and a glass rod moistened with hydrochloric acid held over the liquid, white fumes are formed. Placed under a bell-jar over oil of vitriol, they diminish continually in weight, but without losing their transparency; over quicklime they become somewhat opaque. The hydrated oxide dissolves sparingly in water, but with tolerable facility even in dilute alcohol, and likewise in ether. It has a caustic, penetrating, and persistent taste; blues reddened litmus-paper, and separates ammonia, magnesia, oxide of zinc, &c. from their solutions. Exposed to the air, it quickly absorbs carbonic acid, which cannot be separated from it by quicklime. Its salts, with the exception of the nitrate, are crystallizable, and are all soluble in alcohol and in ether.

Sulphate. — *Preparation* (pp. 93, 94). Crystallizes from the alcoholic solution in beautiful prismatic crystals, which are permanent in the air, and very sparingly soluble in water.

	Dried at 50°.			Löwig.
12 C	72	....	28·45	..... 28·01 to 28·43
15 H	15	....	5·93	..... 5·94 ,, 6·24
2 Sn	118	....	46·60	
O	8	....	3·21	
SO^3	40	....	15·81	..... 15·56 ,, 15·79
$(C^4H^5)^3Sn^2O,SO^3$	253	....	100·00	

Iodide. — *Preparation* (pp. 93–95). To obtain the compound pure, an alcoholic solution of the oxide is agitated with aqueous hydriodic acid, ether, and a quantity of water sufficient to separate the ethereal solution of the iodide, which solution is then evaporated. The iodide then remains, covered with a thin layer of water; and, after the removal of the water, it is treated with a small quantity of chloride of calcium, and after a while decanted.

Transparent, colourless, mobile, strongly refracting liquid, of sp. gr. 1·850; has a very pungent odour, and attacks the eyes and nose like oil of mustard. Boils between 180° and 200°; but nevertheless volatilizes completely when kept for some time over the water-bath. Mixes in all proportions with alcohol and ether; dissolves very sparingly in water, but readily in hydrated alcohol.

				Löwig.		
12 C	72	....	21·75	..... 21·96	.... 22·06	.... 21·83
15 H	15	....	4·53	..... 4·58	.... 4·68	.... 4·71
2 Sn	118	....	35·65			
I	126	....	38·07	.....	37·93 .... 37·55	
$(C^4H^5)^3Sn^2I$	331	....	100·00			

Iodate. — When iodine is added to an alcoholic solution of oxide of methylostannethyl as long as its colour is destroyed, small shining crystals of the iodate separate out, while the iodide remains in solution. The iodate detonates slightly when heated.

Bromide. — Obtained in a similar manner to the iodide, viz., by treating the oxide with hydrobromic acid, or, by saturating the alcoholic solution of the oxide with bromine, agitating with ether and water, and

evaporating the ethereal solution. Sp. gr. 1·630. Resembles the iodide in most of its proporties.

				Löwig.
12 C	72	....	25·26	
15 H	15	....	5·26	
2 Sn	118	....	41·41	
Br	80	....	28·07	..... 27·66
$(C^4H^5)^3Sn^2Br$	285	....	100·00	

Bromate. — Similar to the iodate.

Chloride. — Obtained similarly to the iodide and bromide. It likewise separates immediately on the addition of hydrochloric acid to the alcoholic solution of the sulphate. — Transparent, colourless, strongly refracting liquid, having a more powerful odour and greater volatility than the iodide or bromide. Sp. gr. 1·320. Miscible in all proportions with alcohol and ether.

				Löwig.
12 C	72·0	....	29·95	
15 H	15·0	....	6·24	
2 Sn	118·0	....	49·09	
Cl	35·4	....	14·72	..... 14·55
$(C^4H^5)^3Sn^2Cl$	240·4	....	100·00	

Nitrate. — Obtained by adding dilute nitric acid to the alcoholic solution of the base; agitating with ether; then with a sufficient quantity of water to separate the ethereal solution of the salt; and evaporating the latter. The nitrate then remains as a syrupy mass, which at lower temperatures assumes the form of a transparent, colourless, varnish-like body; it dissolves readily in ether, and burns with a dull light but without detonation. (Löwig.)

				Löwig.
12 C	72	....	26·97	
15 H	15	....	5·62	
2 Sn	118	....	44·19	
O	8	....	3·00	
NO^5	54	....	20·22	..... 20·60
$(C^4H^5)^3Sn^2O,NO^5$	267	....	100·00	

¶ Ethylostannethyl. $(C^4H^5)^6Sn^4$.

For the formation of this compound, see pp. 93, 94.

Oxide. $(C^4H^5)^6Sn^4O$. — Obtained from the sulphate in the same manner as the oxide of methylostannethyl (p. 102). Crystallizes from the alcoholic solution, as a hydrate, in warty nodules. It is a strong base, though not quite so powerful as the oxide of methylostannethyl; has a sharp caustic taste; blues red litmus paper; and separates ammonia from the metallic oxides from their salts. It dissolves sparingly in water;

readily in alcohol and in ether; absorbs carbonic acid rapidly from the air; and forms crystallizable salts readily soluble in alcohol.

	Hydrated Oxide.			Löwig.
20 C	120	30·15		28·00
25 H	25	6·28		6·41
4 Sn	236	59·31		
O	8	2·01		
HO	9	2·25		
$(C^4H^5)^5Sn^4O,HO$	398	100·00		

The hydrate with which the above analysis was made had been kept for some time in the liquid state over the water-bath, and was not quite free from carbonic acid.

Sulphate. — *Preparation* (pp. 93, 94). — Crystallizes from the alcoholic solution in small crystalline needles, which quickly become opaque when exposed to the air, are nearly insoluble in water, and less soluble in alcohol than sulphate of methylostannethyl.

				Löwig.		
20 C	120	27·97	27·31	27·53		27·11
25 H	25	5·82	6·01	5·98		5·75
4 Sn	236	55·03				
O	8	1·86				
SO^3	40	9·32	9·20	9·17		8·91
$(C^4H^5)^5Sn^4O,SO^3$	429	100·00				

Iodide. — Prepared like the iodide of methylostannethyl (pp. 93–95). Thick, oily, colourless liquid, of sp. gr. 1·724. Reduced by potassium and sodium.

			Löwig.	
20 C	120	23·67	23·75	22·90
25 H	25	4·93	5·08	5·21
4 Sn	236	46·55		
I	126	24·85	25·62	26·43
$(C^4H^5)^5Sn^4I$	507	100·00		

This, and the other haloïd compounds of ethylostannethyl, differ from the corresponding compounds of methylostannethyl, only in being more viscid and having a lower specific gravity; in odour, and in their relation to water, alcohol, and ether, they closely resemble the methylostannethyl compounds; and they are prepared by precisely similar processes.

Bromide. — Less viscid than the iodide. Sp. gr. 1·48. Reduced by potassium and sodium.

			Löwig.
20 C	120	26·03	
25 H	25	5·42	
4 Sn	236	51·19	
Br	80	17·36	17·40
$(C^4H^5)^5Sn^4Br$	461	100·00	

The *Iodate* and *Bromate of Ethylo-stannethyl* separate out on adding iodidine or bromine to the alcoholic solution of the oxide.

Chloride. — Resembles the bromide. Sp. gr. 1·30. Reduced by potassium and sodium.

				Löwig.
20 C	120·0	....	28·82	
25 H	25·0	....	6·00	
4 Sn	236·0	....	56·68	
Cl	35·4	....	8·50	..... 8·14
$(C^4H^5)^5Sn^4Cl$	416·4	....	100·00	

Nitrate. — $(C^4H^5)^5Sn^4O,NO^5$. — Prepared like the corresponding salt of methylostannethyl, which it resembles in its properties. (Löwig.)

Six-fourths Stannethyl. $(C^4H^5)^4Sn^6$?

When alcohol was added in small quantities to the dark red ethereal solution of the mass A (p. 93), the liquid became decolorized, and a dark greasy mass separated, which, in two experiments, was found to contain 19·45 and 20·89 p.c. C, and 4·17 and 4·61H, quantities pretty nearly agreeing with the formula $(C^4H^5)^4Sn^6$, which requires 20·43C and 4·25H. — The ethereal solution left to evaporate in the air, yielded a white powder, which dried up to a coherent mass, probably consisting of the oxide of the same radical. Dried at 100°, it yielded 18·12 to 18·60 p.c. C, and 4·18 to 4·33H; the formula $(C^4H^5)^4Sn^6O$, requiring 20·09C, and 4·51H. On dissolving this oxide in hydrochloric acid diluted with alcohol, shaking up the solution with water and ether, and evaporating the ethereal solution, a nacreous salt was obtained, containing 7·20 per cent of chlorine; the formula $(C^4H^5)^4Sn^6Cl$ requires 7·36 p.c. — The original clear ethereal solution often deposited a grey powder, which was scarcely soluble in alcohol and ether; had a pungent odour; and took fire when fuming nitric acid was poured upon it. It appeared to consist of the iodide $(C^4H^5)^4Sn^6I$, its analysis giving 58·8 and 58·6 p.c. Sn, 15·5 C, 3·8 H, and 21·1 I, while the formula requires 59·2 Sn, 16·0 C, 3·5 H, and 21·3 I. But the quantities of these several compounds obtained were too small to render these results of much value. (Löwig.)

¶ Plumbides of Ethyl or Plumbethyls.

Löwig. *J. pr. Chem.* 60, 304; *Ann. Pharm.* 88, 318.

These compounds are formed by the action of iodide of ethyl on plumbide of sodium, containing 1 pt. sodium to 6 pts. lead. On agitating the resulting mass with ether, and evaporating the ethereal solution, there remains a mixture of several plumbides of ethyl, which have not yet been separated from one another, the separation being very difficult, in consequence of the great similarity of their physical properties. — These radicals are perfectly colourless, tolerably mobile, volatile, and have a powerful odour. They do not fume in the air, but when set on fire, they burn and give off dense clouds of oxide of lead. When strong nitric acid is poured upon them, they take fire; and in contact with iodine or bromine, especially with the latter, they explode with violence. They are insoluble in water, but dissolve readily in alcohol or ether. The ethereal or alcoholic solution when exposed to the air, deposits an amorphous powder, which is insoluble in water, alcohol, and ether, and forms crystallizable salts with acids; and in solution there remains a strongly alkaline base, the oxide of *Methyloplumbethyl*, $(C^4H^5)^3Pb^2$ (so

called from its analogy to methyl, C^2H^3), the radical of which constitutes the principal portion of the product obtained by the action of iodide of ethyl on plumbide of sodium.

Oxide of Methyloplumbethyl. $(C^4H^5)^3Pb^2O$. — Obtained as a hydrate by adding a solution of nitrate of silver mixed with alcohol, to the alcoholic solution of the mixed radicals as long as metallic silver is precipitated; filtering from the silver; agitating the resulting solution of nitrate of methyloplumbethyl with alcoholic potash and afterwards with ether; adding a sufficient quantity of water to separate the ethereal solution of the oxide; and evaporating the ether in a retort. Pure hydrated oxide of methyloplumbethyl then remains in the form of a thick oily liquid, which solidifies after a while in a crystalline mass, slippery to the touch like hydrate of potash. It is volatile, and forms white fumes when a rod moistened with hydrochloric acid is held over it. When heated, it gives off white vapours, which excite powerful sneezing, — a property which also belongs to the radical itself and many of its compounds. The hydrate dissolves sparingly in water, readily in alcohol and in ether. The solutions have a strong alkaline reaction; a sharp, disagreeable, caustic taste; and produce an extremely unpleasant sensation in the throat.

Carbonate. — The hydrated oxide rapidly absorbs carbonic acid from the air. By leaving the alcoholic solution of the oxide to evaporate in the air, the carbonate is obtained in small hard crystals. It is nearly insoluble in water, sparingly soluble in alcohol and ether. Alcohol containing hydrochloric acid, dissolves it with effervescence. It has a strong burning taste.

				Löwig.	
13 C	78	24·00		23·93	23·40
15 H	15	4·62		4·74	5·00
2 Pb	208	64·00		63·87	63·74
3 O	24	7·38		7·46	7·86
$(C^4H^5)^3Pb^2O,CO^2$	325	100·00		100·00	100·00

Sulphate. $(C^4H^5)^3Pb^2O,SO^3$. — When sulphuric acid is added by drops to an alcoholic solution of the oxide, leaving the base in excess, a dazzling white crystalline precipitate of the sulphate is obtained, which must be washed with alcohol and afterwards with ether. The salt is nearly insoluble in water, absolute alcohol, and ether, but dissolves readily in alcohol mixed with sulphuric or hydrochloric acid. From the acid solution it crystallizes in tolerably large, hard, shining octohedral crystals.

			Löwig.				
12 C	72	20·90	20·30	20·33			
15 H	15	4·30	4·48	4·60			
2 Pb	208	60·60	61·40	60·30	59·5	60·6	60·4
O	8	2·54	2·08	3·10			
SO^3	40	11·66	11·74	11·67			
$C^{12}H^{15}Pb^2O,SO^3$	343	100·00	100·00	100·00			

Iodide. — $(C^4H^5)^3Pb^2I$? Formed by the action of iodide of potassium on sulphate of methyloplumbethyl. Very instable. When an alcoholic solution of iodide of potassium is added to a solution of the sulphate

acidulated with sulphuric acid, the mixture shaken up with ether, the ethereal solution of iodide of methyloplumbethyl separated by water, and left to evaporate, iodide of lead separates from it in considerable quantity. By rapid evaporation, a colourless oily residue is obtained, having a penetrating odour; and likewise yielding a deposit of iodide of lead. If the compound, while yet undecomposed, be distilled with water, the separation of iodide of lead takes place immediately, and the watery vapour which passes over is accompanied by a colourless, mobile, very pungent liquid, having an odour like that of oil of mustard and no longer subject to spontaneous decomposition. This liquid was found to contain: 25·11 p.c. C, 5·70 H, 36·58 Pb, and 34·16 I, numbers agreeing pretty nearly with the formula $(C^4H^5)^{12}Pb^4I^3$ [or $(Ae^3Pb)^4I^3$], which requires 25·02 C, 5·24 H, 36·40 Pb, and 33·34 I.

Bromide. — Obtained by adding an alcoholic solution of bromide of potassium to a solution of the sulphate in alcohol containing sulphuric acid; agitating the whole with ether; then with water to separate the ethereal solution; and evaporating the latter. The bromide then crystallizes in long needles.

				Löwig.	
12 C	72	19·20			
15 H	15	4·00			
2 Pb	208	55·47			
Br	80	31·33	20·98		21·23
$(C^4H^5)^3Pb^2Br$	375	100·00			

Chloride. — Obtained by adding chloride of barium to a solution of the sulphate in alcohol containing hydrochloric acid; agitating with ether; separating the ethereal solution by water; and leaving it to evaporate. Crystallizes in beautiful, long, needles, having a strong lustre, and giving off a strong odour of oil of mustard when gently heated. When heated in a glass tube, they detonate slightly even at a moderate heat, yielding chloride of lead and metallic lead.

				Löwig.	
12 C	72·0	21·79	21·58		21·51
15 H	15·0	4·54	4·85		4·71
2 Pb	208·0	62·96	62·66		62·74
Cl	35·4	10·71	10·54		10·58
$(C^4H^5)^3Pb^2Cl$	330·4	100·00	99·63		99·54

Nitrate. — Obtained by decomposing the alcoholic solution of the plumbethyls (p. 107.) with nitrate of silver. — On evaporating the alcoholic solution, the salt remains in the form of a colourless, viscid liquid, which smells like butter, has a burning taste, and solidifies after a while in a crystalline, unctuous mass. Decomposed by heat, with slight detonation. Dissolves readily in alcohol and in ether. The alcoholic solution, when slowly evaporated, deposits a small quantity of nitrate of lead. (Löwig.)

			Löwig.	
12 C	72	20·17		
15 H	15	4·20		
2 Pb	208	58·26		
O	8	2·24		
NO^5	54	15·13	14·65	14·89
$(C^4H^5)^3Pb^2O,NO^5$	357	100·00		

¶ Hydrargethyl. $C^4H^5Hg^2$.

STRECKER. *Compt. rend.* 39, 57.
DÜNHAUPT. *Chem. Gaz.* 1854, 263, 292.

Not known in the separate state. Obtained as an iodide by the action of mercury on iodide of ethyl (Strecker); and as a chloride or bromide by decomposing mercuric chloride or bromide with bismethyl (p. 87).

Hydrated Oxide, $C^4H^5Hg^2O,HO$. — Obtained by decomposing a boiling alcoholic solution of the chloride with oxide of silver, filtering, distilling off the alcohol, and evaporating in vacuo. The hydrate then remains in the form of a colourless oil, which is strongly alkaline and burns and blisters the skin. It decomposes the salts of ammonia, but not those of potash or magnesia, and forms precipitates with solutions of alumina, zinc, copper, tin, gold, and platinum. With a large excess of sulphuretted hydrogen, it forms a white precipitate, which after a while turns yellow, brown, and black. — With metallic zinc, it forms zinc-ethyl and amalgam of zinc. It combines with acids, forming crystallizable salts; the carbonate, monobasic phosphate, sulphate, nitrate, acetate, and oxalate have been obtained. (Dünhaupt.)

Carbonate. Prepared by decomposing the chloride with carbonate of silver at a gentle heat. Crystallizes with difficulty, and is easily decomposed by heat. Acids decompose it with evolution of carbonic acid. (Dünhaupt.)

Sulphide. $C^4H^5Hg^2S$. — Sulphide of ammonium added to an alcoholic solution of chloride of hydrargethyl, throws down this compound in the form of a yellowish white pulverulent precipitate, easily soluble in excess of sulphide of ammonium. Dissolves also in alcohol and ether. The alcoholic solution decomposes by evaporation, yielding sulphide of mercury; the ethereal solution yields the compound in the crystalline form with only slight decomposition. It gave by analysis 81·05 p. c. Hg, 8·95 C, 1·96 H, and 6·10 S; the above formula requires 81.63 Hg, 9·79 C, 2·05 H, and 6·53 Hg. (Dünhaupt.)

Iodide. $C^4H^5Hg^2I$. — 1. Obtained by mixing an alcoholic solution of the hydrated oxide with alcoholic iodine as long as the colour of the latter disappears. (Dünhaupt.) 2. By the action of mercury on iodide of ethyl in diffused daylight. (Strecker.) It is decomposed by direct sunshine, and hence Frankland (VIII, 362) failed in obtaining it. — Soluble in boiling ether and alcohol, and separates on cooling in white and very brilliant laminæ. (Dünhaupt, Strecker.) Insoluble in water, but soluble in ammonia and in potash-ley, from which it crystallizes undecomposed. (Strecker.) Volatilizes without decomposition. (Dünhaupt.) Sublimes at 100°, but requires a much stronger heat to melt it. (Strecker.) Yields by analysis, 36·18 p. c. iodine, the formula requiring 35·65. (Dünhaupt.)

Bromide. $C^4H^5Hg^2Br$. — 1. Obtained by mixing the hydrated oxide with hydrobromic acid.—2. By adding an alcoholic solution of bromine to an alcoholic solution of the hydrated oxide till the colour of the bromine becomes permanent: bromate of hydrargethyl is then formed at the same time. — 3. By mixing the alcoholic solutions of bismethyl and mercuric bromide. — Resembles the chloride. Analysis gives 25·84 p. c. Hg; calculation, 25·89. (Dünhaupt.)

Chloride. $C^4H^5Hg^2Cl$. — 1. Precipitated by chloride of sodium from the aqueous solution of the nitrate. (Strecker.) — 2. By the action of protochloride of mercury on bismethyl. (Dünhaupt, p. 87.) Forms light, crystalline iridescent laminæ having a silvery lustre. Sublimes at 40° in thin laminæ without previous fusion, but at 100° it melts to a clear oily liquid, and then evaporates completely. Heated on platinum-foil, it burns with a weak flame, diffusing a very unpleasant odour. It is nearly insoluble in water, dissolves sparingly in ether and in cold alcohol, but freely in boiling alcohol. Analysis gives 76·23 p.c. Hg, 8·73 to 9·62 C, 1·45 to 2·00 H, and 13·67 Cl, the formula requiring 75·63 Hg, 9·06C, 1·90 H, and 13·41 Cl. (Dünhaupt.)

Nitrate. $C^4H^5Hg^2,NO^6$. — Nitrate of silver added to a solution of iodide of hydrargethyl, forms a precipitate of iodide of silver and a solution of nitrate of hydrargethyl, which when evaporated yields the salt in colourless prisms. (Strecker.)

Cyanide. $C^4H^5Hg^2Cy$? — Formed by saturating an alcoholic solution of the hydrated oxide with strong hydrocyanic acid. Crystallizes readily. Very volatile; when heated in a tube, it emits a vapour which has an extremely repulsive odour, attacks the respiratory organs strongly, and appears to be highly poisonous: a carbonaceous residue is left in the tube. The cyanide dissolves readily in alcohol and ether. (Dünhaupt.)

Mercury also forms a compound with methyl, viz:

Hydrargomethyl $C^2H^3Hg^2$. — This compound is obtained in the form of an iodide by the action of metallic mercury on iodide of methyl, under the influence of the solar rays. In about a week, the liquid solidifies in a colourless crystalline mass. By treating this mass with ether, the iodide of hydrargomethyl is dissolved and may thus be separated from the remaining metallic mercury and the small quantity of iodide of mercury formed at the same time. Very little gas is given off during the reaction.

Hydrargomethyl has not yet been obtained in the free state. The *iodide* is a white solid body, insoluble in water, but dissolving pretty readily in alcohol, and very easily in ether and in iodide of methyl. By spontaneous evaporation of either of these solutions, the iodide is obtained in small nacreous, crystalline laminæ. At ordinary temperatures, it is slightly volatile, emitting a peculiar and unpleasant odour; the vapour when inhaled leaves a nauseous taste on the palate, which lasts for several days. At 100°, the iodide is much more volatile, the crystals disappearing completely when exposed to a current of air at that temperature. At 143°, it melts and sublimes without decomposition, condensing in extremely thin, shining, crystalline laminæ. Gives by analysis 3·57 p.c. C, 0·90 H, and 36·56 I, the formula $C^2H^3Hg^2I$ requiring 3·51 C, 0·88 H, and 36·95 I. (Frankland.)

Iodide of hydrargomethyl in contact with ammonia or with the fixed alkalis, is converted into *oxide of hydrargomethyl*, which is dissolved by an excess of either of these reagents; and the solutions thus formed yield with sulphide of ammonium a flocculent precipitate of *sulphide of hydrargomethyl*, having a faint yellowish colour, and a peculiar and most intolerable odour. (Frankland, *Ann. Pharm.* 85, 381.) ¶

B SECONDARY UCLEI.

a. Oxygen Nucleus. C^4H^2 ².

Oxalic Acid. $C^4H^2O^8=C^4H^2O^2,O^6$.

SAVARY. *Diss. de sale acetosellæ. Argentor.* 1773.
WIEGLER. *Crell. Chem. J.* 2, 6.
SCHEELE. *Opusc.* 2, 187.
BERGMAN. *Opusc.* 1, 251; 3, 364 and 370.
WESTRUMB. *Kleine phys. chem. Abh.* 1, 1.
RICHTER. *Neuere Gegenstände,* 8, 92.
THOMSON. *Phil. Trans.* 1808, 63
BÉRARD. *Ann. Chim.* 73, 263; also *A. Tr.* 19, 2, 265.
BERZELIUS. *Gilb.* 40, 250; — *Ann. Chim.* 94, 185;—*Ann. Chim. Phys.* 18, 155; also *Schw.* 33, 422.
F. C. VOGEL. *Schw.* 2, 435 and 7, 1.
DÖBEREINER. *Schw.* 16, 107, and 23, 66.
DULONG. *Mem. de la Classe des Sc. math. et phys. de l'Institut.* Années 1813–14–15, p. cxcix; abstr., *Schw.* 17, 229.
GAY-LUSSAC. *Ann. Chim. Phys.* 46, 218; also *Schw.* 62, 441; also *Ann. Pharm.* 1, 20.
TURNER. *Phil. Mag. Ann.* 9, 161; also *Schw.* 62, 444; also *Br. Arch.* 38, 159. — *Phil. Mag. Ann.*, 10, 348; also *Ann. Pharm.* 1, 22; also *Pogg.* 24, 166.
GRAHAM. Salts. *Ann. Pharm.* 29, 2.
BUSSY. Double Salts. *J. Pharm.* 24, 609; also *Ann. Pharm.* 29, 312; also *J. pr. Chem.* 16, 395.
BERLIN. Double Chromium-Salts. *Berzelius, Jahresbericht.* 24, 244; and more fully: *Berzelius, Lehrb.* Ausg. 5, 3, 1086.
RAMMELSBERG. Crystallo-chemical monograph on Oxalic-acid and its salts. *Pogg.* 93, 24.

Oxalsäure, Kleesäure, Sauerkleesäure, Sauerkleesalzsäure, kohlige Säure, Acide oxalique, Acide carboneux.

History. — Savary in 1773, and Wiegler in 1779, first obtained oxalic acid in the form of a sublimate and an aqueous distillate by heating salt of sorrel. Scheele first prepared it from salt of sorrel by means of subacetate of lead, and showed that the acid thus obtained was identical with the *acid of sugar* previously obtained from sugar and nitric acid, and investigated by Bergman.

Sources. In the free state: In the juice of chick-peas? — In *Boletus sulfureus.* — 2. In oxalate of ammonia: In guano. — 3. As acid oxalate of potash: In *Oxalis acetosella* and *corniculata, Rumex acetosella* and *acetosa,* and *Geranium acetosum;* also in *Spinacia oleracea* and *Phytolacca decandra* (Braconnot), in *Rheum palmatum,* and in the *Herba Belladonnæ.* — 4. As oxalate of soda: In *Salsola Kali* and *Soda,* and in various species of *Salicornia* (*Ann. Pharm.* 16, 86.) — 5. As oxalate of lime: According to Scheele, in *Radix Rhubarb., Alcannæ, Apii, Bistort., Cardo-*

patiæ, Curcumæ, Dictamni albi, Fœniculi, Gentianæ rubræ, Hirundinariæ, Lapathi acuti, Liquiritiæ, Mandragoræ, Ononidis spinosæ, Ireos florent, Ir. nostratis, Rhabarb. suecici, Saponariæ, Scillæ, Sigilli Salam. Tormentillæ, Valerianæ, Zedoariæ and *Zingiberis;* in *Cortex Berberidis, Canell. alba, Cascarill. Cass. caryophyllatæ, Cassiæ fistul., Chinæ, Cinnam., Culibaban, Frangulæ, Fraxini, Quercus, Sambuci, Simarubæ, Ligni sancti* and *Ulmi.* According to others, in *Radix Betæ vulgaris, Corni floridæ, Lathyri tuberosi, Pæoniæ off.,* and *Vincetoxici;* in *Cortex Geoffroyæ Surinamensis* and *Jamaicensis; Kopalki, Quassiæ, Parobo, Pseudochinæ,* and *Winteranus;* in *Lignum Campechiense;* in *Stipites Dulcamaræ;* in *Herba Æsculi Hippocastani, Belladonnæ* and *Mesembryanthemi crystallini.* According to Fourcroy & Vauquelin (*J. Phys.* 68, 429), it occurs in the greater number of plants. According to Braconnot (*Ann. Chim. Phys.* 28, 318; also *Schw.* 45, 156), it constitutes half the substance of many lichens, and by their decay enters into the constitution of the vegetable soil of rocks. — Also in beer-yeast (K. Schmidt). — During the most vigorous period of growth, the oxalate of lime is completely dissolved in the contents of the cells, not through the medium of an acid, for malic and citric acids do not dissolve it, but by the action of vegetable albumin. But towards the end of the period of growth, the oxalate of lime separates in the cells in microscopic square-based octohedrons, *e. g.,* in the cells of *Tradescantia discolor* and of various cacti. (K. Schmidt, *Ann. Pharm.* 61, 297.) — Oxalate of lime occurs in rectangular prisms acuminated with four faces resting on the lateral edges, in the root of *Iris florentina* (Raspail); in *Fritillaria Meleagris, Scilla bifolia* and *maritima, Narcissus, Hyacinthus, and Amaryllis* (Jussieu); in *Piper Magnoliæfolium, Tradescantia, Musa, Calla Ætheopica, Aloë verrucosa,* (Sprengel, Rudolph, and Kieser); in *Crinum latifolium, Mirabilis Jalapa.* (Decandolle, *Mem. de la Soc. d'Hist. Natur.* 4, 223 and 413.) — Oxalate of lime likewise occurs in many urinary calculi (Wollaston); in urinary sediments (Prout); in very small quantity in the urine of the sea-eagle (J. Davy); in the *Liquor Allantoidis* of the cow (Lassaigne); in the mucus of the gall-bladder of men, oxen, dogs, rabbits, and pikes, and in microscopic square-based octohedrons in the mucous membrane of the gravid uterus (K. Schmidt, *Ann. Pharm.* 61, 299); also in the Malpighian vessels of the caterpillar of *Sphinx Convolvuli* (Meckel, K. Schmidt.)—6. As ferrous oxalate: in brown-coal deposits.

Formation. 1. By the action of nitric acid on most organic compounds (VII. 123). — The presence of hydrochloric acid facilitates the formation of oxalic acid. (E. Kopp. *Compt. rend.* 24, 616.) — 2. In the decomposition of cyanogen by water and ammonia (VII. 386, 387). — 3. In the decomposition of uric acid by chlorine, and in the decomposition of the urate of ammonia contained in guano. — 4. When hydrate of potash is fused at a gentle heat with various organic compounds (VII. 135.) Hence Gay-Lussac (*Schw.* 58, 91,) proposes a method (not yet put in practice) of converting tartrate of potash into oxalate. — 5. In the preparation of potassium from carbonate of potash and charcoal (VII. 41).

Preparation. — A solution of acid oxalate of potash (salt of sorrel) in hot water, is treated, according to Scheele's method, with excess of subacetate of lead; and the precipitated oxalate of lead washed, first by frequently pouring water upon it and decanting, the water being renewed every time, and then thoroughly on a cloth filter. It is then digested for

several days, with frequent agitation with a quantity of oil of vitriol sufficient to convert all the lead into sulphate—viz., a little more than 49 pts. oil of vitriol to 68·6 pts. of acid oxalate of potash or 148 pts. of dried oxalate of lead — and diluted with 10 times its weight of water; the aqueous oxalic acid separated from the sulphate of lead by filtration, repeatedly evaporated and cooled, as long as oxalic acid continues to separate; and the product purified by recrystallization from any sulphuric acid that may remain attached to it. — The sulphuric acid may also be removed by digesting the dilute liquid with a small quantity of oxalate of lead, till it no longer forms a cloud with chloride of barium, after which the filtrate must be treated with sulphuretted hydrogen to remove any lead that may have been dissolved. — If the oxalate of lead has not been entirely freed from acetate of potash by careful washing with water, the oxalic acid prepared from it contains acid oxalate of potash, which when ignited remains in the form of carbonate; from this impurity the oxalic acid may be freed by recrystallization, the potash-salt separating out first, — or by sublimation, whereby however a portion of the acid is decomposed. — Anthon (*Repert.* 84, 250) recommends, instead of subacetate of lead, the sulphate which occurs so abundantly as a waste-product in the preparation of acetate of alumina. For this purpose he saturates 1 At. (137·2 pts.) of salt of sorrel in the state of hot aqueous solution, with carbonate of potash; digests the liquid for several days, stirring frequently, with 2 At. (304 pts.) of sulphate of lead; decants the solution of sulphate of potash from the resulting oxalate of lead (which, after thorough washing, should dissolve completely in dilute nitric acid, which it will do if free from sulphate); and decomposes it by continued digestion with 2 At. (98 pts.) of oil of vitriol diluted with a large quantity of water. — Another method is to saturate the salt of sorrel with carbonate of potash, add chloride of barium to throw down oxalate of baryta, and decompose this salt with dilute sulphuric acid.

2. One part of sugar is heated in a retort with 8 pts. nitric acid of sp. gr. 1·2 (1·38, according to Schlesinger), gently at first, but ultimately to the boiling-point; the liquid evaporated in a basin and cooled to the crystallizing point of the oxalic acid; and the mother-liquor repeatedly evaporated, with fresh quantities of nitric acid, as long as crystals separate out on cooling: the crystals are finally purified by recrystallization. (Bergman.) By this process, 3 pts. of sugar and 30 pts. nitric acid of sp. gr. 1·2, yield 1 pt. of oxalic acid. (Bergman.) Instead of pure common sugar, moist sugar may also be used, or the brown syrup of sugar, grape-sugar, or starch. — The nitrous fumes evolved in the process are frequently made available for the preparation of oil of vitriol (II. 180). — If too small a quantity of nitric acid be used, comparatively little oxalic acid is obtained, the chief product being saccharic acid (artificial malic acid), which remains as a thick brown syrup when the liquid is evaporated, but may be converted into oxalic acid by digestion with a larger quantity of nitric acid. — Schlesinger (*Repert.* 74, 24) rightly recommends the use of a larger quantity of nitric acid from the beginning of the operation, so that the crystals of oxalic acid may not be contaminated with a viscid mother-liquor, which can neither be poured off nor absorbed by paper. To 1 pt. of sugar he therefore takes 8 pts. of nitric acid, of sp. gr. 1·38, without further addition of water; evaporates the liquid to $\frac{1}{4}$, after heating it gradually to the boiling-point; and thereby obtains between 58 and 60 pts. of beautifully crystallized oxalic acid from 100 pts. of sugar. If a sufficient quantity of nitric acid has been

used, the colourless or yellowish mother-liquor crystallizes in the form of oxalic acid down to the last drop; but if less nitric acid has been added, the mother-liquor becomes yellow and brown by evaporation, and requires a further addition of nitric acid. Schlesinger likewise recommends that the oxalic acid be recrystallized from water containing a small quantity of nitric acid, and the crystals drained on a funnel, washed with a little cold water, and dried between bibulous paper at a medium temperature. — Oxalic acid prepared with nitric acid is often contaminated with the latter, which may be recognized by the yellow colouring which it imparts to the cork of the bottle in which the crystals are kept. Berzelius removes this nitric acid by allowing the crystals to effloresce in warm air, then recrystallizing from hot water, again leaving them to effloresce, recrystallizing, and so forth.

The crystallized hydrated oxalic acid obtained by (1) or (2) is brought to the anhydrous state (C^2HO^4) by long continued heating over the water-bath, or by sublimation. — Turner first dries the crystallized acid in a basin over the water-bath, covering the basin, first with a sheet of thin bibulous paper, then with a sheet of writing paper, and lastly with a second very shallow basin filled with ice or cold water; he then heats the lower basin to 177° or from that temperature to at most 204°; removes the sublimed needles from the bibulous paper every hour with a feather; and encloses them, while yet warm and before they have absorbed moisture, in a well closed bottle. A small portion of the acid decomposes during this sublimation, and certain products of decomposition are absorbed by the paper. The sublimed acid, when dissolved in water, again yields the common hydrated crystals, showing that the acid has undergone no change by the sublimation. (Turner.)

Properties. As obtained by sublimation: Transparent, colourless, slender, hard needles (Turner); by heating to 100°: White effloresced, pulverulent mass. The acid is a little volatile, even at ordinary temperatures. (Faraday, *Pogg.* 19, 550.) It may be sublimed at 100°; though but slowly; more quickly between 150° and 162°, without any decomposition; but from 165° to 204°, the sublimation goes on more rapidly, and a slight partial decomposition takes place, increasing as the temperature rises. At 212°, the dry acid melts, boils briskly, and evaporates, with partial decomposition. (Turner.) The dry acid neither sublimes nor decomposes when heated to 110° in a retort for two hours, but begins to sublime with partial decomposition between 132° and 150°; it begins to melt at 150°, is completely fused at 180°, and boils at 190°. (Duflos, *Schw.* 62, 450). — The acid is inodorous at ordinary temperatures, but the vapours which it gives off when heated, have a pungent acid odour and excite sneezing and coughing. (Turner.) Its taste is more intensely sour than that of any other organic acid; and in rather large quantities *e.g.* half an ounce, it acts as a deadly poison. In its power of reddening litmus, it likewise surpasses all other organic acids. Its solution in 2000 pts. of water still exhibits this reaction. When heated with oil of vitriol, it gives off carbonic acid and carbonic oxide in equal volumes. Its solution produces a cloud in a few minutes in an aqueous solution of gypsum.

		Or:		*Dry Oxalic acid.*	Gay-Lussac & Thénard.	Berthollet.
2 C	12	4 C	24	26·67	26·57	25·13
H	1	2 H	2	2·22	2·74	3·09
4 O	32	8 O	64	71·11	70·69	71·78
C^2HO^4	45	$C^4H^2O^3$	90	100·00	100·00	100·00

Gay-Lussac & Thénard, and likewise Berthollet, analysed oxalate of lime dried at 100°, which may be regarded either as CaO,C^2HO^4, or as $2CaO,C^4H^2O^8$.

The formula C^2HO^4, which represents oxalic acid as a monobasic acid, is supported by the following considerations: 1. That this formula is the more simple of the two. — 2. That oxalic acid may be formed from cyanogen, C^2N, that is to say, from a compound containing only 2 At. C. — 3. That indigotic acid, which contains 14C, is converted by nitric acid into picric acid containing 12C, and oxalic acid, for which therefore there remain but 2C from the indigotic acid. — 4. That the formulæ of many oxalates are simpler on this view.

The formula $C^4H^2O^8$, which represents the acid as bibasic, is in accordance with: 1. The even number of atoms. (VII. 198.) — 2. The boiling point (*ibid.*) — 3. The great tendency of the acid to form acid and double salts. — 4. The fact that formic acid, $C^2H^2O^4$, and wood-spirit, $C^2H^4O^2$, are not converted into oxalic acid by oxidation with nitric acid. (Gm.) On the other hand, formic acid, which is a compound of a lower order, may be formed from oxalic acid. — 5. That oxalic acid may be converted into oxamic acid, $C^4H^3NO^6$, whose formula cannot be halved; moreover the relation between this acid and oxalic acid is too close to admit of the supposition that oxalic acid contains 2C and oxamic acid 4C. (Laurent.) — 6. If oxalic ether be regarded as C^4H^5O,C^2O^3, its vapour will be monatomic; but if its formula be $2C^4H^5O,C^4O^6$, its vapour will be diatomic, like those of other compound ethers of the third order. (Laurent.)

The radical-theory, besides the acid dried as completely as possible *per se*, assumes the existence of a hypothetically anhydrous oxalic acid $= \dot{O} = C^2O^3$, containing therefore 33·33 per cent. C, and 66·67 O, as it may be supposed to exist in the metallic oxalates and the oxalic ethers. According to this view, oxalic acid dried *per se* is not C^2HO^4 (or $C^4H^2O^8$), but HO,C^2O^3 (or $2HO,C^4O^6$), therefore a hydrate of oxalic acid.

Decompositions. 1. The acid passed through a *red-hot* tube, is completely resolved into water and gaseous products, without deposition of charcoal. — 2. The acid, when *heated* in a basin or a retort, volatilizes, without leaving any carbonaceous residue, partly undecomposed, partly resolved into water and equal volumes of carbonic oxide and carbonic acid gases, partly into carbonic and formic acids. (Gay-Lussac.) Equation for the first decomposition:

$$C^4H^2O^8 = 2CO + 2CO^2 + 2HO;$$

for the second:

$$C^4H^2O^8 = 2CO^2 + C^2H^2O^4.$$

The acid containing water of crystallization melts in a retort at 98°, and gives off, even at 100°, together with vapour of water and formic acid, a mixture of carbonic oxide and carbonic acid gases in the proportion by volume of 5 : 6; this evolution of gas increases considerably between 120° and 130°, and continues till all the oxalic acid has disappeared; towards the end of the process, the proportion of carbonic acid becomes somewhat greater, and the last portions of water which pass over contain the greatest quantity of formic acid. If the heat be not too violent, all the oxalic acid volatilizes in the decomposed state. (Gay-Lussac.) — Oxalic acid containing water of crystallization melts at 98°, is tranquil at

110°; gives off but a trace of gas at 126°, and but very little even at 132°. It boils at 143°, giving off, with the watery vapour, only a small quantity of gas, which however becomes abundant between 155° and 160°, and, as found by Gay-Lussac, contains 5 vol. carbonic oxide to 6 vol. carbonic acid. Oxalic acid previously dehydrated begins to decompose and give off gas at 165°; if the heat be gradually applied, the gas thus evolved contains 5 vol. carbonic oxide to 6 vol. carbonic acid; but, if the heat be quickly raised, the proportion of carbonic oxide decreases (Turner; compare Duflos, *Schw.* 62, 450; Schlesinger, *Repert.* 74, 31.) — The products of decomposition are the same, whether the acid be heated in a retort alone, or in contact with spongy platinum or pumice-stone; but the addition of charcoal powder produces a great disturbance in the decomposition. (Reiset & Millon, *N. Ann. Chim. Phys.* 8, 290.) — Bergman had previously shown that oxalic acid when heated, melts, boils, and sublimes, partly undecomposed, partly resolved into a gaseous mixture consisting half of carbonic acid, and half of a gas which burns with a blue flame. — Oxalic acid is not, strickly speaking, *combustible*, but the carbonic oxide evolved from it in a red-hot crucible may of course be set on fire.

3. Aqueous oxalic acid is very slowly oxidized by platinum-black, — if that substance contains oxygen — and converted into water and carbonic acid (Döbereiner, *Ann. Pharm.* 14, 14.)

4. Dehydrated oxalic acid absorbs dry *chlorine gas*, and forms with it, without evolution of gas, a white substance which is resolved by water into hydrochloric and carbonic acid. The acid containing water of crystallization is immediately decomposed by chlorine, yielding hydrochloric and carbonic acid; 1 vol. chlorine produces 2 vol. carbonic acid. (Döbereiner.) Hence the dry compound is probably $C^4H^2O^8Cl^2$, and on addition of water yields $4CO^2$ and 2HCl. Also when chlorine is passed through the aqueous acid, complete decomposition ensues, with formation of carbonic and hydrochloric acid. (Anthon, *Repert.* 59, 342.)

5. *Bromine* added to aqueous oxalate of potash or soda containing a slight excess of alkali, does not act in the cold; but between 40° and 50°, pure carbonic acid gas is abundantly evolved and a metallic bromide formed. (Cahours, *N. Ann. Chim. Phys.* 19, 486; also *J. pr. Chem.* 41, 61):

$$C^4K^2O^8 + 2Br = 4CO^2 + 2KBr.$$

6. By continued digestion with *Nitric acid*, oxalic acid is completely decomposed [yielding carbonic acid and water]. (Bergman.) Schlesinger's more recent statement (*Repert*, 74, 33) that oxalic acid is not decomposed by boiling nitric acid is unfounded; but at all events the decomposition takes place but slowly. (Gm.) ¶ According to Reinsch (*Jahrb. pr. Pharm.* 18, 189), a solution of effloresced oxalic acid in moderately heated fuming nitric acid yields, on cooling, a number of crystals having a glassy lustre, easily decomposible, and containing equal numbers of atoms of oxalic and nitric acid? ¶

7. With aqueous *Hypochlorous acid*, oxalic acid gives off carbonic acid and chlorine; if the former acid is strong and the latter crystalline, violent frothing takes place attended with evolution of heat.

8. Oxalic acid heated with aqueous *Iodic acid* is decomposed, with evolution of carbonic acid and liberation of iodine (H. Davy):

$$5C^4H^2O^8 + 2IO^5 = 20CO^2 + 10HO + 2I.$$

Periodic acid acts in a similar manner, but the decomposition is slow even at a boiling heat. (Benckiser, *Ann. Pharm.* 17, 258.) — With 1 pt. of hydrated oxalic acid to 2 pts. iodic acid dissolved in 10 to 100 pts. water, no action takes places at 10° in 20 hours; at 18° or 20°, iodine separates out in 3 or 4 hours; and the decomposition is complete in 4 or 5 days; at 60° it is completed in a few minutes, with violent effervescence. — Light has also great influence on this reaction. If two equal portions of the mixture be taken, and placed for two hours,at 19°, the one in the dark, the other in sunshine (from 9 to 11 o'clock), the quantities of gas evolved by the two are as 1 : 12; and in the more powerful sunshine of 11 to 1 o'clock, the proportion is 1 : 18. Moreover there is as much carbonic acid evolved in sunshine at 10°, as in diffused daylight at 25°. — Spongy platinum likewise accelerates the decomposition. If the temperature is so low that the mixture of the two acids evolves no gas, the introduction of spongy platinum immediately causes an evolution of gas. If a mixture which evolves gas be divided into two portions, and spongy platinum introduced into one of them, this portion will yield in a given time 25 or 30 times as much gas as the other. The evolution of gas increases with the quantity of spongy platinum, but not in the same ratio; with 5 and 10 grammes of spongy platinum, the quantities of gas evolved are as 3 : 4. Platinum plates having a surface of 84 square centimetres do not increase the evolution of gas; they become covered with bubbles which prevent their further action. — Charcoal likewise accelerates the evolution of gas, considerably at first, but after a short time more feebly, so that on the whole the quantity of carbonic acid given off is only doubled. — The proportion of the oxalic to the iodic acid has no influence on the rapidity of the decomposition, provided only that the quantity of the latter be sufficient to decompose the oxalic acid, that is to say, at least 332 pts. (2 At.) iodic acid to 630 pts. (5 At. hydrated) oxalic acid. The reaction is likewise unaffected by the degree of dilution with water. — On the other hand, the reaction between the two acids, even between 60° and 80°, is prevented by the presence of very small quantities of hydrocyanic acid. If to a solution of 1 grm. of hydrated oxalic acid in 5 grammes of water there be added one drop of 15 per cent. prussic acid, and then a solution of 2 grm. iodic acid in a small quantity of water, no action is perceptible even for 14 days; by that time however the hydrocyanic acid is exhausted and iodine separates out. For, in the decomposition of oxalic by iodic acid, there are two stages to be distinguished: 1. Oxidation by the iodic acid alone; 2. Oxidation assisted by the iodine set free in the first stage. The former of these actions is very trifling, and takes place even in presence of hydrocyanic acid; the second is very strong, but does not take place in presence of hydrocyanic acid, because this acid immediately converts the liberated iodine into iodide of cyanogen and hydriodic acid, and the latter, when hydrocyanic acid is present, does not act upon iodic acid in such a manner as to form water and iodine. But when hydrocyanic acid is absent, this last-mentioned reaction takes place; and consequently, the decomposition of oxalic acid by iodic acid may be accelerated by adding a small quantity of hydriodic acid, which throws down iodine and thereby facilitates the action. — Ferrocyanide and ferricyanide of potassium do not interfere with the reaction. (Millon, *N. Ann. Chim. Phys.* 13, 31; also *J. pr. Chem.* 35, 13.)

9. Oxalic acid heated with oil of vitriol is resolved into water, which

remains behind, and a mixture of carbonic oxide and carbonic acid gases in equal volumes. (Döbereiner.)

$$C^4H^2O^8 = 2HO + 2CO + 2CO^2.$$

Dehydrated oxalic acid decomposes with brisk effervescence in contact with fuming oil of vitriol, even at ordinary temperatures. The hydrated acid dissolves in oil of vitriol, and decomposes on the application of a gentle heat. (Döbereiner.) — The decomposition of hydrated oxalic acid by common oil of vitriol begins between 110° and 115°. (Gay-Lussac.) The dehydrated acid is decomposed by common oil of vitriol slowly at 100°, quickly at 110°; the hydrated acid exhibits moderate effervescence at 104°, if the oil of vitriol is in very large excess. (Turner.) — 1 pt. of hydrated oxalic acid heated with 10 pts. of purified oil of vitriol begins at 123°, to give off gas free from formic acid; a mixture of 1 pt. hydrated oxalic acid with 4 pts. sulphuric acid of sp. gr. only 1·4, begins to boil at 122°; and as soon as, by evaporation of the water, the boiling point has risen to 134°, a slight evolution of gas takes place, becoming rapid at 143°, and ceasing at 155°. The gaseous mixture produced at 134° contains 11 vol. carbonic oxide to 12 vol. carbonic acid; that which is given off at 155° contains the two gases in equal volumes; the distillate contains nothing but formic acid, amounting to rather more than ½ per cent of the hydrated oxalic acid used. (Duflos.) — When 1 pt. hydrated oxalic acid is heated with 10 pts. *Phosphoric acid* of sp. gr. 1·3, similar phenomena are produced; the evolution of gas begins at 140°, ceases at 163°, and the distillate contains formic acid, amounting to ½ per cent of the hydrated oxalic acid.

10. Aqueous oxalic acid reduces, with formation of carbonic acid and water: chromic acid to chromic oxide (vanadic acid to vanadic oxide, *Berzelius*), and the peroxides of manganese, lead, cobalt, and nickel to salifiable bases, with which the undecomposed portion of the oxalic acid combines, (Döbereiner):

$$2C^4H^2O^8 + 2MnO^2 = C^4Mn^2O^8 + 4CO^2 + 4HO.$$

Compare Winkelblech, *Ann. Pharm.* 13, 167. — When 4 pts. of dehydrated oxalic acid are saturated with 21 pts. of peroxide of lead, the mass instantly rises to a red heat. Hydrated oxalic acid mixed with an equal or a double quantity of peroxide of lead, becomes strongly heated, with formation of aqueous vapour, carbonic acid gas, and carbonate of lead, but does not exhibit incandescence. (Böttger, *J. pr. Chem.* 8, 477; *Beiträge*, 2, 39.) — If the oxalic acid is mixed with chromic acid or one of the above-named peroxides, and with sulphuric acid at the same time, it is completely resolved into carbonic acid and water, with formation of a metallic sulphate. (Döbereiner):

$$C^4H^2O^8 + 2MnO^2 + 2SO^3 = 4CO^2 + 2HO + 2(MnO,SO^3).$$

11. Oxalate of ammonia mixed with aqueous *Protochloride of Mercury* is decomposed under the influence of light, yielding sal-ammoniac, calomel, and carbonic acid. (Planche, *J. Pharm.* 1, 62.) Probably thus:

$$2NH^3,C^4H^2O^8 + 4HgCl = 2NH^4Cl + 2Hg^2Cl + 4CO^2.$$

The mixture of the saturated solutions remains clear in the dark; in daylight it becomes turbid in six minutes, and in the course of an hour deposits calomel, which in sunshine quickly falls down in soft flakes,

surrounded with bubbles of carbonic acid gas. The filtrate no longer contains mercury, but sal-ammoniac and undecomposed oxalate of ammonia. (Planche.)

12. *Teroxide of Gold*, in contact wih aqueous oxalic acid, is quickly reduced to the metallic state, with evolution of carbonic acid. From an aqueous solution of chloride of gold, oxalic acid throws down all the gold in the metallic state, slowly in the dark, more quickly under the influence of light, the decomposition being attended with evolution of carbonic acid. (Pelletier.)

13. Oxalic acid and its salts added to the aqueous solution of *Bichloride of Platinum*, precipitate the metal under the influence of sunshine, with evolution of carbonic acid (Döbereiner, *Schw.* 62, 94). Kemp (*Repert.* 74, 236), who perhaps did not expose the mixture to the sun, states that no precipitation takes place.—The aqueous solution of *chloriridiate of Ammonium* is not decomposed by oxalic acid at a boiling heat; but on exposure to sunshine, it is completely decolorized, with evolution of carbonic acid and precipitation of grey metallic iridium. (Döbereiner.)

14. Salt of sorrel heated with *Hydrate of Potash*, is resolved into hydrogen gas and carbonate of potash. (Péligot, *Ann. Chim. Phys.* 73, 133):

$$C^4HKO^8 + 3(KO,HO) = 4(KO,CO^2) + 2HO + 2H.$$

Similarly when heated with *Hydrate of Baryta*, it yields hydrogen gas and colourless alkaline carbonate (Dumas & Stas, *Ann. Chim. Phys.* 73, 123; Pelouze & Millon):

$$C^4HKO^8 + 3(HO,BaO) = KO,CO^2 + 3(BaO,CO^2) + 2HO + 2H.$$

15. Anhydrous normal oxalates heated with dry *Baryta*, yield carbonic oxide gas and carbonate of baryta. (Pelouze & Millon, *Ann. Pharm.* 33, 182):

$$C^4M^2O^8 + 2BaO = 2(BaO,CO^2) + 2MO + 2CO.$$

16. *Potassium* and *Sodium* decompose dehydrated oxalic acid at a gentle heat, with vivid combustion, yielding charcoal and alkali [and hydrogen gas]. (Gay-Lussac & Thénard.)

Combinations. With *Water.*

a. Hydrated Oxalic acid. Commonly called crystallized oxalic acid; but the dehydrated acid is also crystalline — The dehydrated acid becomes heated by contact with water; when exposed to the air, it quickly absorbs as much water as the hydrated crystals had lost on being heated (Richter); hence the sublimed needles of the dehydrated acid quickly become opaque on exposure to the air. (Turner.) The crystals which separate from the aqueous solution by evaporation or cooling, always consist of the hydrated acid.—(*Preparation*, p. 112.)

Large, transparent, colourless prisms belonging to the oblique prismatic system, fig. 95; the *a*-faces may however be wanting. Cleavage parallel to *u* and *u'*; $i : u$ or $u' = 98° 30'$; $u : u' = 63° 5'$, $i : c = 129° 20'$; $i : l$ [backwards *l*] $= 103° 15'$; $i : a = 107°$. The faces *i*, *c*, and *f* appear as faces of a six-sided prism, and the faces *u* and *a* as acumination-faces of the same. (Brooke, *Ann. Phil.* 22, 119.) Sometimes also the *u*-faces are very predominant $u : u'$ [probably backwards] $= 116° 52'$; $u : f = 117° 2'$, $i : c = 129° 20'$; $c : f = 127° 26'$; $c : f$ backwards $= 103° 24'$; *a* above : *a* below $= 145° 24'$; $a : u = 140° 19'$. (Prevostaye, *N. Ann. Chim. Phys.*

453); see also Rammelsberg (*Pogg.* 93, 25). — The crystals placed er burnt lime within a bell-jar not exhausted of air, do not give off ater at ordinary temperatures, even in the course of several hours; t at 21° they effloresce on the surface. (Turner.) At 100°, they slowly ive off all their water on exposure to the air.—Sp. gr. of the crystals ·641. (Joule & Playfair, *Chem. Soc. Qu. J.* 1, 121.)

		Thomson.	Bérard.	Berzelius.	Bergman.	Richter.
$C^4H^2O^8$	90	71·43	77	72·7	71·5	70	69·7
4 Aq	36	28·57	23	27·3	28·5	30	30·3
$C^4H^2O^8+4Aq$	126	100·00	100	100·0	100·0	100	100·0

Or:		Prout.	Hermann.
4 C	24	19·05	19·04	19·4
6 H	6	4·76	4·76	4·7
12 O	96	76·19	76·20	75·9
	126	100·00	100·00	100·0

b. Aqueous Oxalic Acid. The crystals of the hydrated acid dissolve in 8 pts. of cold water, forming a thin, transparent, and colourless liquid of sp. gr. 1·045. (Richter.) They dissolve in 15·5 pts. of water at 10°, in 9·5 pts. at 13·9°; in very small quantities at 100°, and at the boiling point of the solution, which is considerably above 100°, in almost any proportion, inasmuch as, even at 104·5, they deliquesce in their water of crystallization. (Turner.) Oxalic acid contaminated with nitric acid, dissolves in 2 pts. of cold water. (Berzelius.) The crystals sometimes decrepitate as they dissolve in water.

Oxalic acid dissolves in *hydrochloric* and in *dilute sulphuric* acid, without decomposition.

Oxalates. Oxalic acid is one of the strongest acids, and in its affinity for certain bases, lime for example, exceeds even the strongest mineral acids. — When common salt is distilled with aqueous oxalic acid, a large quantity of hydrochloric acid is evolved. (Berthollet, *Statique Chim.* 1, 271.) Dry chloride of sodium or chloride of calcium intimately mixed with hydrated oxalic acid, gives off all its hydrochloric acid when heated, so that the residue left after ignition consists of carbonate of soda or carbonate of lime. (A. H. Wood, *Phil. Mag. J.* 5, 445; compare Kobell (*J. pr. Chem.* 14, 379.) Oxalic acid decomposes aqueous hydrochlorate or nitrate of soda, acid oxalate of soda crystallizing out. (Döbereiner, *J. pr. Chem.* 15, 317.) — The solution of dehydrated oxalic acid in absolute alcohol does not decompose carbonate of potash or carbonate of lime, but the carbonates of baryta, strontia, and magnesia, are decomposed by it; it also dissolves nitrate of lime dissolved in absolute alcohol. (Pelouze.)

Normal oxalates in their driest state, in which however they cannot all be obtained are $= C^4M^2O^8$; the *acid* oxalates $= C^4HMO^8$; the *hyperacid* oxalates $= C^4HMO^8, C^4H^2O^8$; there are also basic oxalates. If oxalic acid be regarded as C^2HO^4, the normal salts will be $= C^2MO^4$, the acid salts $= C^2MO^4, C^2HO^4$; and the hyperacid salts $= C^2MO^4, 3C^2H^4O^4$, according to which formula they may be distinguished, as *monoxalates, bioxalates,* and *quadroxalates.* According to the formula, $C^4H^2O^8$, adopted in this work, they might be distinguished as dioxalates, monoxalates, and bioxalates; this nomenclature, however, we shall not adopt, as it would lead to confusion of terms. — Dulong regards the anhydrous normal salts (C^2MO^4 or $C^4M^2O^8$) as compounds of a metal with carbonic acid.

The anhydrous normal oxalates of the fixed alkalis are resolved, by gentle ignition out of contact with the air, into carbonic oxide gas and alkaline carbonates; those of the earths, and of those heavy metallic oxides which retain their oxygen with the greatest tenacity, such as manganous oxide, into a mixture of carbonic oxide and carbonic acid gases in equal volumes, and a residue of oxide; and those of other heavy metals, into carbonic acid gas and a residue of metal. The lead-salt gives off 3 vol. carbonic acid to 1 vol. carbonic oxide, and suffers partial reduction :

$$C^4K^2O^8 = 2CO + 2(KO,CO^2)$$
$$C^4Mg^2O^8 = 2CO + 2CO^2 + 2MgO$$
$$C^4Cu^2O^8 = 4CO^2 + 2Cu$$
$$C^4Pb^2O^8 = CO + 3CO^2 + Pb^2O.$$

The oxalates of mercury, silver, and platinum exhibit slight detonation when thus decomposed. — Oxalates when thus heated in a close vessel leave little or no carbon, and are thereby distinguished from the salts of most other organic acids. The very small quantity of charcoal which the oxalates of the earths and fixed alkalis often leave, whereby the residue acquires a greyish tint,—or at least a slight greyish or brownish shade is imparted to the substance during the ignition,—is attributed by Berzelius (*Lehrb.*), to organic impurities, and by H. Rose (*Pogg.* 9, 26), to the fact that some of the water present is decomposed [but this should produce the contrary effect, inasmuch as the oxygen of the water would then contribute to the combustion of the carbon].

The oxalic acid contained in oxalates exhibits many of the above-mentioned reactions of the free acid. Thus, oxalates heated with oil of vitriol give off carbonic acid and carbonic oxide in equal volumes. Alkaline oxalates dissolved in water are converted by platinum-black into carbonates. (Döbereiner, *Ann. Pharm.* 14, 14.) When boiled with aqueous chloride of gold, they throw down metallic gold. — Potassium decomposes many anhydrous oxalates with loud explosion.

Most normal oxalates are insoluble in water; a few dissolve in aqueous oxalic acid and sal-ammoniac; all in dilute nitric acid, but less readily than most other salts of organic acids which are insoluble in water. Oxalates dissolved in water precipitate all dissolved lime-salts, even gypsum, unless a strong mineral acid be present in considerable excess; the precipitate is insoluble in acetic acid and in sal-ammoniac.

Oxalate of Ammonia. — *a. Normal.* 1. Obtained by neutralizing the acid with ammonia or carbonate of ammonia. — 2. By decomposing oxalate of lead with hydrosulphate of ammonia which has been prepared by precipitating aqueous sulphide of barium with carbonate of ammonia and distilling the filtrate (Liebig, *N. Tr.* 18, 2, 260). — Long prisms united in tufts, and belonging to the right prismatic system. *Fig.* 78; without distinct directions of cleavage; $p : u$ or $u' = 90°$; $p : i = 143° 30'$; $i : i = 107°$; $i : t = 126° 30'$; $u' : u = 104° 6'$; $u' : m = 142° 3'$; $u' : t = 127° 57'$; u : *the face above* $m = 121°$. (Brooke, *Ann. Phil.* 22, 374; *compare* Prevostaye, *N. Ann. Chim. Phys.* 4, 453; (see also Rammelsberg. (*Pogg.* 93. 29.) — Very slightly volatile at ordinary temperatures. (Faraday, *Pogg.* 19, 552.) Has the taste of sal-ammoniac. Sp. gr. of the crystals = 1·5. (Joule and Playfair, *Chem. Soc. Qu. J.* 1, 121.)

Dried.			Berzelius.		Bérard.		Thomson.
$2\,NH^3$	34	27·42	26·88		27·66		25·55
C^4O^6	72	58·06	59·37		72·34		74·45
$2\,HO$	18	14·52	13·75				
$C^4(2NH^4)O^8$	124	100·00	100·00		100·00		100·00

Crystallized.			Berzelius.	Bérard.		Rammelsberg.
$2\,NH^3$	34	23·94	87·4	87	50·78	50·07
C^4O^6	72	50·71				
$4\,HO$	36	25·35	12·6	13		
$C^4(2NH^4)O^8+2Aq$	142	100·00	100·0	100		

The crystals effloresce when heated, giving off 2 At. water. At a higher temperature, the dry residue is resolved, with partial fusion, and leaving at most a trace of charcoal, partly into carbonic oxide, carbonic acid, ammonia, and water, partly into oxamide and water; part of it also yields hydrocyanic acid, and if the distillation be interrupted at the proper time, oxamic acid is likewise found in the residue. The decomposition may, perhaps, be represented by the following equations:

$$C^4N^2H^8O^8 = 2CO + 2CO^2 + 2NH^3 + 2HO.$$

$$C^4NH^5O^8 = \underbrace{C^4N^2H^4O^4}_{\text{oxamide.}} + 4HO.$$

$$C^4N^2H^8O^8 = 2CO^2 + C^2NH + NH^3 + 4HO.$$

[Respecting the oxamic acid, vid. acid oxalate of ammonia.]

A small portion only of the salt sublimes undecomposed [or rather in the form of oxamide], the greater part yielding carbonate of ammonia (Bergman), together with carbonic oxide and water. (Berzelius.) When carefully heated, it yields carbonate of ammonia and carbonic oxide gas free from carbonic acid. (Mitchell, *Sill. Am. J.* 25, 344.) — If the heat be maintained at 220°, the salt is wholly resolved into carbonic oxide and carbonate of ammonia, without any formation of oxamide. (Malaguti, *Compt. rend.* 22, 852.) Oxalate of ammonia in combination with cerous or manganous oxalate, yields hydrocyanic acid when heated, in addition to carbonic oxide, carbonic acid, ammonia, and water. (Döbereiner, *Repert.* 15, 425.) — The anhydrous salt melts and boils only where it is in contact with the hot parts of the retort, giving off: first ammonia; then a mixture of carbonic oxide and carbonic acid (the former predominating in the beginning, because a large quantity of carbonic acid enters into combination with the ammonia, afterwards in equal volumes, and ultimately mixed with cyanogen gas [vapour of hydrocyanic acid?]); then carbonate of ammonia, with 4 or 5 per cent of oxamide, which partly sublimes, partly passes over into the watery distillate, so that the oxamide floats therein in white flakes: there remains a trace of charcoal. (Dumas, *Ann. Chim. Phys.* 44, 129; also *J. Chim. méd.* 6, 401; also *Schw.* 61, 82; also *Pogg.* 19, 474.) A small quantity of oxamic acid is also formed at the same time, because the residue, by evolution of ammonia, is partly converted into acid oxalate of ammonia. (Balard.) The salt, even when dissolved in hot water, gives off ammonia, and acquires the power of reddening litmus. (Emmett.) The aqueous solution of the salt is decomposed in the circuit of the voltaic battery, yielding carbonic acid at the

positive, and ammonia and water at the negative pole. (Daniell, *Ann. Pharm.* 36, 35):

$$C^4N^2H^8O^8 = 4CO^2 + 2NH^3 + 2H.$$

The aqueous solution becomes alkaline, when exposed to the light for half a year. (Horst, *Br. Arch.* 4, 257.) The salt heated with $\frac{1}{8}$ to $\frac{1}{4}$ its weight of oil of vitriol, yields carbonic oxide and carbonic acid in equal volumes, and sulphate of ammonia. (Gall. *Phil. Mag. J.* 6, 232.) — This statement of Gell's contradicts that of Mitchell (*Sill. Am. J.* 25, 344), who finds that, in this decomposition, carbonic oxide free from carbonic acid is given off, together with carbonate of ammonia, and nothing remains but strong sulphuric acid. — The salt dissolves in about 20 pts. of cold water, but not in alcohol.

b. Acid-salt.—1. Precipitated in the crystalline form from the aqueous solution of the normal salt, by oxalic, sulphuric, hydrochloric, or nitric acid. — ¶ 2. A hot aqueous solution of 1 At. oxalic acid and 1 At. chloride of ammonium deposits this salt on cooling. (Anderson, *Chem. Soc. Qu. J.* I. 231.) ¶. — Yields crystals belonging to the right prismatic system. *Fig.* 68, but generally without the *y*-face, and on the other hand, with the *m*-face. $p : i = 150° 47'$; $p : t$ or $m = 90°$; $u : m = 155° 37'$; $u : t = 114° 23'$; $i : t = 119° 13'$. (Prevostaye, *N. Ann. Chim. Phys.* 4, 453). — The salt tastes sour, reddens litmus, and is less soluble in water than the normal salt. — Sp. gr. of the crystals, 1·613. (Joule & Playfair.)

	Dehydrated.				Bérard.
NH^3	17	....	15·89	.....	16·05
C^4O^6	72	....	67·29	.....	83·95
2 HO	18	....	16·82		
$C^4(H,NH^4)O^8$	107	....	100·00	.....	100·00

	Crystallized.			Bérard.	Rammelsberg.
NH^3	17	....	13·60	14·00	14·12
C^4O^6	72	....	57·60	58·72	57·75
4 HO	36	....	28·80	27·28	28·13
$C^4(H,NH^4)O^8+2Aq$	125	....	100·00	100·00	100·00

The crystallized salt yields by dry distillation, first water; then carbonic oxide and carbonic acid gases, a large quantity of formic acid and oxamide; afterwards carbonate and hydrocyanate of ammonia; and if the heat be then discontinued, the residue consists of oxamic acid $C^4NH^3O^6$. (Balard.) The crystals, when gently heated, effloresce from loss of water, sometimes undergoing the aqueous fusion at the same time. At a higher temperature, the solidified mass becomes viscid; between 220° and 230° it becomes pasty, and begins to decompose with strong intumescence; gives off a mixture of carbonic acid with a smaller quantity of carbonic oxide gas; and yields a distillate containing a large quantity of formic acid, together with a small sublimate of oxamide. At a higher temperature, when the disengagement of gas ceases, a yellow bitter substance is produced, and a mixture of hydrocyanate and carbonate of ammonia is evolved, which effervesces with the acid distillate previously passed over. If the process be then interrupted, there remains in the retort a porous,

ellow mass (or brown, if too much heat has been applied) of c acid, possibly mixed with small quantities of oxamide and unaltered oxalate of ammonia. The dry salt, $C^4NH^5O^8$, is resolved into H^3O^6 and 2HO. (Balard, *N. Ann. Chim. Phys.* 4, 93; also *Ann. m.* 42, 196; also *J. pr. Chem.* 25, 84.)

. *Hyperacid Salt.* Crystallizes from the aqueous solution of equal s of hydrated oxalic acid and crystallized acid oxalate of ammonia. crystalline form and in composition, it resembles the corresponding ash-salt (Graham), exhibiting only a slight difference in the angles. revostaye.) The crystals effloresce at 100°, giving off 15·4 per cent At.) of water. They dissolve readily in hot water. (Rabourdin, *N. J. harm.* 6, 187.) Specific gravity of the crystals, 1·652. (Joule & layfair.)

Dried at 100°.				Rabourdin.
8 C	48	24·36		24·18
N	14	7·11		7·32
7 H	7	3·55		3·61
16 O	128	64·98		64·89
$C^4(H,NH^4)O^8,C^4H^2O^8$	197	100·00		100·00

Crystallized.				Rabourdin.
8 C	48	20·60		20·44
N	14	6·01		5·99
11 H	11	4·72		4·69
20 O	160	68·67		68·88
$C^4(H,NH^4)O^8,C^4H^2O^8+4Aq$	233	100·00		100·00

Oxalate of Potash.—a. Normal.—Salt of sorrel is heated with water and carbonate of potash, till the liquid becomes slightly alkaline; the solution is then filtered and cooled to the crystallizing point. According to Wenzel, the crystals are rhombic and six or more-sided prisms with oblique dihedral summits; according to Prevostaye (*N. Ann. Chim. Phys.* 4, 453, the memoir being accompanied by a figure of the crystals), they belong to the oblique prismatic system and exhibit a complicated form. ¶ According to Rammelsberg, they are octohedrons belonging to the oblique prismatic system, (vid. *Pogg.* 93, 27, where the measurements of the angles are given.) ¶. — The crystals have a cooling bitter taste and effloresce when heated. (Bergman.) They contain 2 At. water. At 100°, they quickly become opaque, but do not give up all their water till heated to 160°; in a moist atmosphere, the dry residue again takes up 10·63 per cent of water. (Graham.) As Bérard found much more water in the crystals, it would appear that there are two kinds to be distinguished. The dry salt leaves carbonate of potash when ignited. Mixed with an equal weight of pulverized antimony and ignited for 10 minutes in a covered crucible at the heat of a blast furnace, it leaves antimony containing potassium. The crystals dissolve in 3 pts. of cold water. (Thomson.) Sp. gr. of the bihydrated crystals=2·127. (Joule & Playfair.)

Dehydrated.			F. C. Vogel.	Thomson.
2 KO	94·4	56·73	55·78	55·13
C^4O^6	72·0	43·27	44·22	44·87
$C^4K^2O^8$	166·4	100·00	100·00	100·00

	Graham's Crystals.			Rammelsberg.
2 KO	94·4	51·19		50·85
C^4O^6	72·0	39·05		38·49
2 HO	18·0	9·76		
$C^4K^2O^8 + 2Aq$	184·4	100·00		

	Bérard's Crystals.			Bérard.
2 KO	94·4	42·83		42·12
C^4O^6	72·0	32·67		32·46
6 HO	54·0	24·50		25·42
$C^4K^2O^8 + 6Aq$	220·4	100·00		100·00

b. Acid Salt. — *a.*—*Salt of Sorrel, Sauerkleesalz, Sal Acetosellæ, Oxalium.* — Obtained from the jnice of various species of *Oxalis* and *Rumex*, by evaporation, clarifying, crystallization, and recrystallization, or by partially saturating with carbonate of potash the oxalic acid produced by the action of nitric acid on sugar or syrup. — The hydrated crystals, which are permanent in the air and have a sour and bitterish taste, belong to the oblique prismatic system, *Fig.* 114, the edge between *a* and *a* being replaced by the *i*-face. $i : t = 133° 26'$; $i : m = 90°$; $i : u = 132°$; $i : a = 130° 35'$; $u : a = 127° 50'$; $u : m = 103° 38'$; $t : m = 90°$ (Prevostaye). The crystals yield by dry distillation, 1 per cent of a white acid sublimate [dry oxalic acid?] and 31 per cent of colourless water containing oxalic acid (a small quantity of oxalic and a large quantity of formic acid, according to Döbereiner, *Schw.* 63, 222,) and leave 33·3 per cent of a light grey residue, consisting of carbonate of potash with 0·4 per cent of charcoal. (Wiegleb.) — Salt of sorrel adulterated with cream of tartar leaves a considerable quantity of charcoal; according to Dumas, it likewise blackens and gives off sulphurous acid when heated with oil of vitriol. — The crystals dissolve sparingly in cold water, in 14 pts. of boiling water, and in 34 pts. of boiling alcohol. (Wenzel.) Sp. gr. of the aqueous solution saturated at 8° = 1·014. — Sp. gr. of the crystals = 2·044. (Joule & Playfair.)

	Crystallized.			Graham.	F. C. Vogel.
KO	47·2	32·28		32·23	31·44
C^4O^6	72·0	49·25		49·38	55·93
3 HO	27·0	18·47		18·39	12·63
$C^4HKO^8 + 2Aq$	146·2	100·00		100·00	100·00

¶. *β.* According to Rammelsberg (*Pogg.* 93, 32), the salt obtained by saturating a certain quantity of oxalic acid with carbonate of potash and then adding an equal quantity of oxalic acid, forms crystals belonging to the right prismatic system, and containing only half as much water as the preceding.

				Rammelsberg.	
2 KO	94·4	35·54	36·41	35·22	35·36
2 C^4O^6	144·0	54·28	55·31	54·32	54·00
3 HO	27·0	10·18			
$2C^4HKO^8 + Aq$	265·4	100·00			

or, according to Rammelsberg: $2(KO,2C^2O^3) + 3Aq$.

γ. Rammelsberg also, in preparing potassio-antimonic oxalate (*q. v.*), obtained another hydrate containing $\frac{2}{3}$ as much water as *α*, or $\frac{4}{3}$ as much

as β. This salt is more soluble than the ordinary hydrate [α or β?], from the solution of which it might perhaps be obtained by crystallization at lower temperatures. Its crystalline form is also different, and the crystals effloresce very quickly.

				Rammelsberg.
KO	47·2	34·37		34·58
C^4O^6	72·0	52·50		51·93
2 HO	18·0	13·13		
Antimonic oxide				1·05
$C^4HKO^8 + Aq$	137·2	100·00		

Or: $KO,2C^2O^3 + 2Aq$. The crystals were contaminated with a small quantity of adhering antimonic oxide, which could not be separated from them. (Rammelsberg.) ¶

c. *Hyperacid Salt.* — Discovered by Savary and Wiegleb; more minutely examined by Wollaston, (*Phil. Trans.* 1808, 99.) — According to Bérard, it is sometimes sent into the market instead of salt of sorrel [when the latter is prepared from oxalic acid and carbonate of potash.] — Precipitated on adding oxalic, sulphuric, hydrochloric, or nitric acid to the saturated aqueous solution of normal or acid oxalate of potash; it is also produced by mixing an aqueous solution of chloride of potassium with oxalic acid. — Very acid needles. (Wiegleb.) Complicated crystals, often of great size, belonging to the doubly oblique prismatic system (Prevostaye, *N. Ann. Chim. Phys.* 4, 453, where a figure of the crystals is given together with the magnitudes of the angles. Sp. gr. 1·849 (Joule & Playfair.) The crystals give off 13·43 per cent of water at 128°. (Berzelius.) The residue, when more strongly heated, gives off part of the oxalic acid without decomposition, the rest in the decomposed state, and leaves carbonate of potash. The carbonate of potash left by 3 pts. of this salt exactly neutralizes 1 pt. of the undecomposed salt. (Wollaston.) — The salt is still less soluble in water than the salt *h*. According to Pohl (*J. pr. Chem.* 56, 216), 1 pt. of the salt dissolves at 20·6°, in 20·17 pts. of water.

Anhydrous.		
KO	47·2	21·63
2 C^4O^6	144·0	65·99
3 HO	27·0	12·38
$C^4HKO^8,C^4H^2O^8$	218·2	100·00

Crystallized.			Bérard.	Rammelsberg.
KO	47·2	18·57	18·95	18·24
2 C^4O^6	144·0	56·65	57·64	55·73
3 HO	27·0	10·62	23·41	
4 Aq	36·0	14·16		
$C^4HKO^8,C^4H^2O^8 + 4Aq$	254·2	100·00	100·00	

Oxalate of Potash and Ammonia. — 146·2 pts. [1 At.] of salt of sorrel with 19 pts. [17 pts = 1 At.] ammonia form long needles permanent in the air. (Wenzel.) — ¶. The solution subjected to fractional crystallization, first yields crystals having the form of neutral oxalate of ammonia, and containing that salt in large excess; but afterwards the proportion of the ammonia-salt diminishes, and ultimately crystals are obtained nearly free from ammonia and having the form of neutral oxalate of potash. The third crop of crystals obtained from such a solution contained 34·55 p. c. (=22 At.) oxide of ammonium to 2·76 p. c.

(1 At.) potash, and the next crop, which had the form of the potash-salt, contained only 1 At. NH^4O to 60 At. KO. Similar results are obtained by neutralizing binoxalate of ammonia with potash. Hence it appears that there is no definite oxalate of potash and ammonia, but that the two salts merely crystallize together in isomorphous mixtures, taking the form sometimes of one, sometimes of the other salt, the ammonia salt, from its inferior solubility, greatly predominating in the earlier crystallizations. (Rammelsberg, *Pogg.* 93, 30.) ¶

Oxalate of Soda.. — *a. Normal.* — Obtained by neutralizing 1 pt. of hydrated oxalic acid with 2 pts. of decahydrated carbonate of soda. Small crystalline grains, permanent in the air. They turn violet-juice green; have but little taste; are converted into the acid salt by the stronger acids; are very slightly soluble in water, and insoluble in alcohol. (Bergman.) — ¶. 1 pt. of oxalate of soda dried at 100° dissolves at 21·8° in 26·78 pts. water, and at the boiling point of the solution in 16·02 water (Pohl); in 36·4 pts. of water of ordinary temperature, and 24·6 pts. of boiling water. (Rammelsberg.) ¶. These crystalline grains leave 79·01 per cent of carbonate of soda when ignited, and are therefore anhydrous. (Graham.) Bérard, who found in the crystals only 41·08 per cent, and Thomson, who found only 31·08 per cent of soda, appear to have examined a hydrated crystallized salt.

	Crystallized.			Graham.
2 NaO	62·4	....	46·43	46·33
C^4O^6	71·0	....	53·57	
$C^4Na^2O^8$	134·4	....	100·00	

b. Acid. — Obtained by neutralizing a certain quantity of oxalic acid with carbonate of soda, — heating with water at the same time, and then adding an equal quantity of the acid. Also by dissolving 1 At. oxalic acid and 1 At. chloride of sodium in hot water and leaving the solution to cool. (Anderson.) — The crystals redden litmus. In vacuo over oil of vitriol, they lose somewhat more than 1 per cent, but near upon 160° they lose 14·64 per cent (somewhat more than 2 At.) water, and leave when ignited 40·67 p. c. carbonate of soda (Graham); 40·9 p. c. (Bérard.)

	Crystallized.			Bérard.	Graham.	Rammelsb.
NaO	31·2	....	23·96	23·99	23·84	23·88
C^4O^6	72·0	....	55·30	57·90		54·11
HO	9·0	....	6·91	18·11		
2 Aq	18·0	....	13·83			
$C^4HNaO^8 + 2Aq$	130·2	....	100·00	100·00		

Oxalate of Soda and Potash. — Salt of sorrel neutralized with soda yields crystals resembling alum, not deliquescent; they dissolve easily in water and then separate out in efflorescent masses. (Wenzel.) — ¶ According to Rammelsberg, on the contrary (*Pogg.* 79, 562), a boiling solution of salt of sorrel neutralized with carbonate of soda, yields on cooling (or by evaporation, if dilute) a crystalline pulverulent salt, which is not a double salt of soda and potash, but ordinary oxalate of soda, $C^4Na^2O^8$. ¶

Oxalate of Lithia. — *a. Normal.* — Crystallizes with difficulty in small opaque nodules, which dissolve readily in water. — *b. Acid.* —

Transparent, crystalline granules, somewhat less soluble than the normal salt. (C. Gmelin.)

Oxalate of Baryta. — *a. Normal.* — *a. With* 2 *At. Water.* — Precipitated in the form of a white tasteless powder, on mixing oxalic acid with excess of baryta-water, or normal oxalate of potash with the aqueous solution of a baryta-salt. It is not dehydrated by being heated above 100°; but when subjected to dry distillation, yields water, carbonic oxide, carbonic acid, a hydrocarbon, and an empyreumatic oil, leaving a residue of carbonate of baryta mixed with charcoal. (Dulong.) — It dissolves in 200 pts. of cold water, and in an equal quantity of hot water. (Bucholz, *Taschenb.* 1818, 188.) — Dissolves much more readily in a cold aqueous solution of sal-ammoniac. (Brett, *Phil. Mag. J.* 10, 95; Wackenroder, *Ann. Pharm.* 41, 315.)

		Bérard.	Thomson.	Graham.
2 BaO	153·2	63·00	62·17	62
C^4O^6	72·0	29·60	37·83	38
2 HO	18·0	7·40		
$C^4Ba^2O^8 + 2Aq$	243·2	100·00	100·00	

¶ *β. With* 1 *At. water* — Separates immediately on mixing a concentrated solution of chloride of barium with a very small quantity of oxalic acid. Forms very small crystals undistinguishable by the naked eye, but appearing under the microscope as very regular sharp-edged prisms. Very sparingly soluble in water. (W. Wicke, *Ann. Pharm.* 90, 108.)

			Wicke.
2 BaO	153·2	65·42	65·18
C^4O^6	72·0	30·74	
HO	9·0	3·84	
$C^4Ba^2O^8 + Aq$	234·2	100·00	

b. Acid Salt. — When carbonate, hydrochlorate, or nitrate of baryta is mixed with excess of aqueous oxalic acid, the filtrate on cooling yields transparent crystals, which, when boiled with water, are resolved into the insoluble salt *a*, and an acid liquid, from which crystals of the salt *b*. separate on cooling. (Bergman.) — A concentrated solution of chloride of barium mixed with oxalic acid yields needles; a dilute solution remains clear. (Gm.) 100 pts. of the salt obtained from carbonate of baryta, yield, when boiled with water, a quantity of oxalic acid equal to that which is contained in the undissolved normal salt. The acid salt yields by ignition, a quantity of carbonate of baryta containing 45 per cent of baryta. (Bérard.) — When carbonate of baryta is treated with excess of oxalic acid, and the resulting salt simply washed with cold water till it has lost its sour taste, it yields by ignition 59·82 per cent of baryta, not much more therefore than the normal salt. The salt thus obtained is therefore the normal salt, having merely a small quantity of free oxalic acid adhering to it; neither is an acid salt obtained by digesting the normal oxalate with free oxalic acid; hence the acid oxalate appears not to exist. (Graham.) — ¶ When saturated solutions of oxalic acid and chloride of barium are mixed in equal quantities, no turbidity is produced at first; but in about a minute, crystals of the acid oxalate begin to form in abundance. These crystals are acute rhombic laminæ. They dissolve in 336 pts. of water at 15·5°, forming an acid solution; are decomposed by hot water; converted into the normal oxalate by alkaline solutions; and

are not altered by alcohol or ether. After drying in vacuo, they suffer no loss of weight at 100°; at 177°, they give off water; at 204°, oxalic acid; and at higher temperatures they evolve carbonic acid and leave carbonate of baryta. (Clapton, *Chem.. Soc. Qu. J.* 5, 223.) — Chloride of barium added to excess of oxalic acid yields an acid oxalate of baryta, which by slow evaporation may be obtained in beautiful pointed crystals several lines long. Dissolves sparingly in cold, more readily in warm water, and is precipitated from its aqueous solution by alcohol. (W. Wicke.) ¶

				Bérard.
BaO	76·6	43·62		45·0
C^4O^6	72·0	41·00		
3 HO	27·0	15·38		
$C^4HBaO^8 + 2Aq$	175·6	100·00		

			Clapton.	Wicke.
BaO	76·6	45·98	45·86	45·94
C^4O^6	72·0	43·22	39 03	
2 HO	18·0	10·80	12·65	
$C^4HBaO^8 + 4Aq$	166·6	100·00	97·54	

Bérard's determination of the baryta agrees better with the second of the above formulæ than with the first.

Oxalate of Strontia. — *a. Normal.* — *a. With* 2 *At. Water.* — Formed by precipitating nitrate of strontia with normal oxalate of potash. White tasteless powder. (Hope.) — When heated above 100°, it still retains water, and at higher temperatures evolves the same products as the baryta-salt. (Dulong.) — Dissolves in 19·20 pts. of boiling water. (Hope.) — Dissolves sparingly in cold, easily in hot aqueous solutions of hydrochlorate of ammonia, and still more readily in nitrate of ammonia. (Brett.)

	Air-dried.		Bérard.	Vauquelin.	Thomson.
2 SrO	104	53·61	54·46	59·5	60·23
C^4O^6	72	37·11			
2 HO	18	9·28			
$C^4Sr^2O^8 + 2Aq$	194	100·00			

¶ *β. With* 6 *At. Water.* — On adding oxalic acid to excess of nitrate of strontia, or nitrate of strontia to excess of oxalic acid, a crystalline salt is obtained, which, under the microscope, appears to consist of very beautiful, transparent, square-based octohedrons: the crystalline character is also quite perceptible to the naked eye. (Wicke.)

			Wicke.
2 SrO	104	45·21	45·13
C^4O^6	72	31·31	
6 HO	54	23·48	
$C^4Sr^2O^8 + 6Aq$	230	100·00	¶

b. Acid Salt. — Thomson obtained a salt contaning 43·1 per cent of strontia. According to Bérard, the salt *a* is but very slightly soluble in aqueous oxalic acid. — Oxalic acid and salt of sorrel form with aqueous

nitrate of strontia, even in tolerably dilute solutions, a crystalline pulverulent precipitate, concerning which it is not known decidedly, whether it is the normal or the acid salt. — ¶ Concentrated solutions of oxalic acid and chloride of strontium immediately yield crystals, consisting of broad rhombic tables and small octohedrons, the proportion of strontia in which is intermediate between that of the normal and that of the acid salt. (Clapton.) — According to Wicke, the acid oxalate of strontia does not exist, the salt obtained by adding oxalic acid to nitrate of strontia or *vice versa*, being a neutral oxalate (*vid sup.*). ¶

Oxalate of Lime. — Occurs in various parts of plants and animals, as mentioned on page 112. — Precipitated when a solution containing lime is mixed with any compound of oxalic acid, provided there be no strong mineral acid present in large excess, and no alumina, chromic oxide or ferric oxide. — White, tasteless powder, which, according to Bergman, turns violet-juice green at a boiling heat; or transparent crystals, such as Fourcroy (*Crell. Ann.* 1794, 1, 460) obtained by evaporating the solution of the salt in nitric acid. — In vegetable and animal structures, the microscope shows the presence of crystals of this salt, formed by the combination of a square prism with a square-based octohedron (*Fig.* 29). — Sometimes the square octohedron is the primary form (*e*:*e* over the vertex = 46° 28′); sometimes an obtuse octohedron (*e*:*e* over the vertex = 119° 34′.) (*K. Schmidt.*) — Raspail describes the same crystals as rectangular prisms acuminated with four faces resting on the lateral edges at an angle of 162° 20′ to 162° 55′. — When oxalate of lime is formed by double decomposition, even in very dilute solutions, a powder is obtained, consisting of extremely small crystals, too small indeed for measurement; but the solution of oxalate of lime in hydrochloric acid, evaporated at temperatures between 30° and 40°, yields large rhombic tables resembling cholesterin (angle of the rhombus = 79° 33′), which are perhaps a hydrated acid salt, and likewise, on the edge of the watch-glass, crystals of *Fig.* 29, in which *e*:*e* over the vertex = 119° 30′. On evaporating the liquid, the rhombic tables fall to pieces, being resolved into a heap of numerous square-based octohedrons. (K. Schmidt, *Ann. Pharm.* 61, 304.) — Upon and between some metastatic crystals of calcspar from Hungary, there were found crystals having a strong lustre like that of sulphate of lead; they were recognized by Sandall as hydrated oxalate of lime. $C^4Ca^2O^8$, 2Aq. Their density is 1·833; they are very brittle, have a conchoïdal fracture, and are softer than calcspar. Their primary form is an oblique rhombic prism. (*Fig.* 81.) Cleavage parallel to *i*, *u*, and *t*. They likewise exhibit the faces *a*, *a*, *f*, *t*, a face replacing the lateral edge between *t* and *u*, and the face *x*. — i : *a* = 127° 25′; i : *u* = 143° 4′; *i* : *f* backwards = 109° 28°; *i* : *t* = 90°; *a* : *a* = 143° 18′; *a* : *t* = 142° 36′; *a* : *u* = 142° 15′; *u* : *u* = 100° 36′; *u* : *t* = 129° 42′. Macle-crystals often occur. (Brooke, *Phil. Mag.* p. 16, 449.) — [Even if the crystallographic descriptions of Raspail and Schmidt can be easily reconciled, by considering Raspail's rectangular prism as a square prism, the form described by Brooke is certainly quite different, perhaps from a difference in the quantity of water.]

	Dried above 100°.		F. C. Vogel.
2 CaO	56	43·75	43·75
C^4O^6	72	56·25	56·25
$C^4Ca^2O^8$	128	100·00	100·00

Dried at 100°.			F. C. Vogel.	Bérard.	Thomson.
2 CaO	56	38·35	38·5	38	37·5
C^4O^6	72	49·32	49·5	62	62·5
2 HO	18	12·33	12·0		
$C^4Ca^2O^8+2Aq$	146	100·00	100·0	100	100·0

Dried at 38°.			Thomson.
2 CaO	56	34·15	33·98
C^4O^6	72	43·90	43·69
4 HO	36	21·95	22·33
$C^4Ca^2O^8+4Aq$	164	100·00	100·00

According to Graham, also the salt dried at a gentle heat, = $C^4Ca^2O^8$ + 4Aq.; and at the temperature of 100° gives off in 2 days, 13·27, and in 6 days 15·25 per cent, or more than 2 At. of water. Above 100°, the salt gives off the last 2 At. water, but recovers them again on exposure to the air. (F. C. Vogel.)—After drying at 150°, it becomes on the slightest disturbance, so highly electrical, that it is thrown out of the containing vessel; it even retains this property when cold, till it has again absorbed water. (Berzelius.) — According to Dulong, the salt dried at 100°, yields by dry distillation the same products as the baryta-salt; according to Berzelius and others, it is resolved into water, carbonic oxide and carbonate of lime. — Potassium or sodium, heated with the salt to the melting point of the metal, forms alkali and charcoal, with a faint appearance of combustion. (Gay-Lussac & Thénard, *Recherches.*) — Strong potash-solution separates oxalic acid from oxalate of lime; but lime, on the other hand, takes the oxalic acid from a dilute solution of oxalate of potash. (K. Schmidt, *Ann. Pharm.* 61, 304.) A similar reciprocity therefore to that which is exhibited, by lime carbonic acid, and potash (I. 128.) — Oxalate of lime boiled with carbonate of potash [or soda] is gradually decomposed, yielding carbonate of lime and oxalate of potash. (Scheele.) — The solution of oxalate of lime in nitric acid yields crystals of oxalic acid when evaporated. (Braconnot, *N. Ann. Chim. Phys.* 17, 353.)

Oxalate of lime is insoluble in water, aqueous solution of sal-ammoniac (Scheele), (even at a boiling heat, according to Brett, Hünefeld & Wackenroder), and in aqueous acetic acid. (Scheele.) — It is quite insoluble (Scheele, Moretti) or very sparingly soluble (Bérard) in aqueous oxalic acid; slightly in aqueous lactic acid (Cap & Henry); dissolves with tolerable facility in aqueous hydrochloric or nitric acid, whence it may be precipitated by caustic ammonia or potash or their oxalates. Chloride of manganese likewise renders oxalate of lime slightly soluble in water. (Turner, *Pogg.* 19, 148.) — ¶ Oxalate of lime immersed in a solution of a cupric salt (*e. g.* the sulphate, chloride, or nitrate) is gradually converted into cupric oxalate, a soluble lime-salt being formed at the same time. In presence of a large quantity of chloride of sodium, calcium, or ammonium, oxalate of lime dissolves completely in solution of protochloride of copper; but if the solution be agitated or left to stand for some time, cupric oxalate separates out. When oxalate of lime is boiled with a soluble salt of silver, lead, cadmium, zinc, nickel, cobalt, strontia or baryta, a soluble lime-salt is formed, and an oxalate of the other base is precipitated. (A. Reynoso, *Compt. rend.* 29, 527.) ¶

Oxalate of Lime with Chloride of Calcium. — The saturated solution of oxalate of lime in warm concentrated hydrochloric acid yields on cooling

of crystals, which must be pressed between bibulous paper, till no longer exhibit any acid reaction. They are permanent in the give off 23·9 per cent of water when heated to 100° in a dry current r, and 34·35 per cent (10 At.) at 130°; mere traces between 130° 200°, but still continue to give off water when gradually heated from to 250°, at which temperature the evolution of water ceases; the l quantity given off is 34·22 p.c. (14 At.) The crystals, which have w become opaque, absorb water again from the air, without deliquescing, d dissolve in hydrochloric acid without effervescence, showing that ey have not been decomposed by the heat. But when treated with ater, even in the smallest quantity, they are immediately resolved into oluble chloride of calcium and insoluble oxalate of lime. (Fritzsche, *Pogg.* 28, 121.)

	Crystallized.		Fritzsche.
$C^4Ca^2O^8$	128·0	35·09	35·27
2 CaCl	110·8	30·37	30·35
14 Aq	126·0	34·54	34·38
$C^4Ca^2O^8$,2CaCl + 14Aq	364·8	100·00	100·00

Oxalate of Magnesia. — Magnesia takes oxalic acid from the soluble alkalis. (Bergman.) This salt is formed by digesting carbonate of magnesia with aqueous oxalic acid, or by precipitating the aqueous solution of a magnesia-salt with normal oxalate of potash. The latter mixture, when left at rest, does not deposit the oxalate of magnesia till after a considerable time, but if strongly agitated, deposits it in a few seconds. (Gay-Lussac, *Ann. Chim. Phys.* 70, 431.) The same compound separates from a mixture of the aqueous solutions of sulphate or hydrochlorate of magnesia and salt of sorrel, hyperacid oxalate of potash remaining in solution. (Graham.) — White powder. — The air-dried salt, which contains 4 At. water, loses after drying for several days over the water-bath, only 2·32 per cent, and at 148°, altogether 3·42 per cent of water; the remaining portion of water appears not to go off without decomposition of the salt. (Graham.) — At a red heat, the salt leaves magnesia free from charcoal. (Bergman.) — It is but very slightly soluble in water, and even on the addition of oxalic acid, becomes scarcely more soluble, according to Bérard, and according to Graham not at all.

			Bérard.	Graham.	Thomson.
2 MgO	40	27·03	27·35	27·59	26·32
C^4O^6	72	48·65			
4 HO	36	24·32			
$C^4Mg^2O^8$ + 4Aq	148	100·00			

Bérard examined the salt dried at 100°, Graham the air-dried salt.

Oxalate of Magnesia and Ammonia. — *a. With excess of the Ammonia-salt.* — Obtained by saturating a concentrated solution of normal oxalate of potash with oxalate of magnesia, keeping it boiling for a considerable time, — or by saturating acid oxalate of ammonia in a similar manner with magnesia (whereupon oxalate of magnesia separates out), and filtering hot. As the filtrate cools, the double salt separates in milk-white nodules, which effloresce in the air and dissolve both in hot and in cold water, but not without some degree of turbidity arising from the separation of oxalate of magnesia. (G. A. Kayser, *Pogg.* 60, 143.)

	Crystallized.			Kayser.
5 NH^3	85	21·14		21·59
MgO	20	4·98		4·02
3 C^4O^6	216	53·73		53·11
9 HO	81	20·15		
$2[C^4(2NH^4)O^4] + C^4(Mg,NH^4)O^8 + 4Aq$	402	100·00		

Kayser supposes the salt to contain: $6NH^3$, 1MgO, $7C^2O^3$, and 10Aq.

b. With excess of Magnesia-salt. — An aqueous mixture of hydrochlorate of magnesia and normal oxalate of ammonia remains clear for a while, but when concentrated, deposits the double salt in a few hours, and if dilute, in the course of days or weeks, in the form of a white, slightly translucent, tasteless, crystalline crust, requiring more than 480 pts. of water to dissolve it. (Brandes, *Schw.* 27, 18.) The formation of this salt takes place with peculiar facility when the mixture contains excess of ammonia. The salt swells up considerably when heated. (Bonsdorff.) From its solution in hydrochloric or nitric acid, it is not reprecipitated by ammonia. (Berzelius, *Lehrb.*)

	Crystallized.			Brandes. (*approx.*)
NH^3	17	6·86		9
3 MgO	60	24·19		25
2 C^4O^6	144	58·06		58
3 HO	27	10·89		8
$C^4(NH^4,Mg)O^8, C^4Mg^2O^8 + 2Aq$	248	100·00		100

Oxalate of Magnesia and Potash. — Formed by boiling a concentrated solution of normal oxalate of potash with excess of recently precipitated oxalate of magnesia, and filtering hot. As the liquid cools, milk-white nodules are produced, which effloresce rapidly in the air, are nearly insoluble in cold water, but dissolve in hot water, with separation of oxalate of magnesia. (Kayser.)

	Crystallized.			Kayser.
KO	47·2	24·43		25·59
MgO	20·0	10·35		10·89
C^4O^6	72·0	37·27		
6 HO	54·0	27·95		27·62
$C^4KMgO^8 + 6Aq$	193·2	100·00		

When magnesia is digested with salt of sorrel, a small quantity dissolves, but quickly separates out again as oxalate of magnesia, without forming a double salt. (Graham.)

Cerous Oxalate. — Oxalic acid and alkaline oxalates added to cerous salts throws down hydrated cerous oxalate in the form of a white powder, which, when heated in a close vessel, gives off water, carbonic oxide, and carbonic acid, and leaves a mixture of ceroso-ceric oxide, with a small quantity of carbide of cerium. (Berzelius.) The salt, when prepared with cerous oxide free from lanthanum, contains 6 At. water, which it does not part with completely even at 260°. When more strongly heated, it leaves a black powder which takes fire in the air, and burns till it converted into ceric oxide. (Beringer, *Ann. Pharm.* 42, 143.) The salt is insoluble in water and in aqueous oxalic acid. (Berzelius.) It dissolves without decomposition in hot nitric acid, and crystallizes out again on cooling.

Dried in vacuo over oil of vitriol.			Beringer.
2 CeO	108	46·14	45·90
C^4O^6	72	30·78	29·60
6 HO	54	23·08	24·50
$C^4Ce^2O^8 + 6Aq$	234	100·00	100·00

Ceric Oxalate. — Insoluble in water, but soluble in aqueous solution of sal-ammoniac. This solution, when evaporated first deposits a yellowish powder, and then yields lemon-yellow crystals. (Berzelius.)

Potassio-cerous Oxalate, C^4KCeO^8. — White powder insoluble in water and leaving, when ignited, a mixture of ceroso-ceric oxide and carbonate of potash. (Berzelius, *Lehrb.*)

Oxalate of Lanthanum. — Insoluble in water. (Mosander.)

¶ *Oxalate of Didymium.* — Pulverulent and white, with a slight tinge of rose-colour, when precipitated from neutral solutions; but when redissolved by the aid of heat in excess of nitric or hydrochloric acid, it separates as the liquid cools, in the granular and crystalline state, sometimes even in small, rose-coloured, rectangular prisms terminated by four-sided pyramids with their faces resting on the edges of the prism. This salt is completely insoluble in water, and nearly insoluble in oxalic acid and in very dilute mineral acids. After drying in the air, it gives off about 20 per cent of water at 100°. (Marignac, *N. Ann. Chim. Phys.* 38, 175.)

Dried at 100°.			Marignac.
2 DiO	112	55·45	55·53
C^4O^6	72	35·64	
2 HO	18	8·91	
$C^4Di^2O^8 + 2Aq$	202	100·00	

Air-dried.			Marignac.
2 DiO	112	43·75	44 to 45
C^4O^6	72	28·12	
8 HO	72	28·13	
$C^4Di^2O^8 + 8Aq$	256	100·00	¶

Oxalate of Yttria. — Oxalic acid precipitates salts of yttria. (Klaproth.) The precipitate, which at first is bulky and curdy, shrinks together after awhile, assuming a snow-white colour. It does not give off its 6 At. water till it begins to decompose; at a red heat, it leaves pure yttria free from carbonic acid. (Berlin.) The salt is insoluble in water, but dissolves in acids somewhat more readily than the cerous salt. (Gahn and Berzelius.) It is insoluble in aqueous oxalic acid and in dilute hydrochloric acid, but dissolves in nitric and in strong hydrochloric acid. (Berlin.)

			Berlin.
2 YO	64	33·68	
C^4O^6	72	37·90	
6 HO	54	28·42	26·12
$C^4Y^2O^8 + 6Aq$	190	100·00	

¶ The preceding description applies strictly, not to pure oxalate of yttria, but to mixture of the oxalates of yttria, erbia, and terbia. These three salts, however,

resemble each other very closely, but the yttria-salt is more soluble in acids than the oxalates of erbia and terbia; and on this property is founded a method of separating yttria from the other two earths (*vid.* III, 291). ¶

Oxalate of Yttria and Potash. — Precipitated, as a heavy white powder, on mixing an yttria-salt with normal oxalate of potash or with salt of sorrel. (Berzelius, Berlin, H. Scheerer, *Pogg.* 56, 207.) Contains yttria and potash in equal numbers of atoms. (Berlin.) When ignited it leaves a mixture of yttria and carbonate of potash. Insoluble in water. (Berzelius.)

Oxalate of Glucina. — Remains, when its aqueous solution is evaporated, in the form of a transparent gummy mass, possessing the sweetest taste of all glucina-salts. (Vauquelin.)

Oxalate of Alumina. — *a. Normal.* Insoluble in water; its formula, according to Berzelius, is $Al^2O^3,3C^2O^3$ [$=C^{12}Al^4O^{24}$.] Gehardt & Laurent assume the existence of another aluminum, $Al\beta=\frac{2}{3}$ Al (VII. 409), and translate $Al^2O^3,3C^2O^3$ into $C^4Al\beta^2O^6$.

b. Acid. The solution of hydrate of alumina in aqueous oxalic acid leaves on evaporation, a transparent, yellowish, amorphous, sweetish, astringent mass, which reddens litmus but not violet-juice. Swells up in the fire, and deliquesces in the air. (Bergman.) The solution does not precipitate hyposulphate of lime. (Herschel.)

Oxalate of Alumina and Potash. — By dissolving 1 pt. of hydrate of alumina in 5 pts. of salt of sorrel and evaporating, a gummy mass is obtained which remains dry in the air, but is easily soluble. (Wenzel.)

Oxalate of Alumina and Soda. — The filtered solution of hydrate of alumina in aqueous acid oxalate of soda, yields, when slowly evaporated, especially if covered with a layer of alcohol, thin laminæ, which readily give off their water of crystallization at 100°, and when ignited leave a mixture of alumina and carbonate of soda. They contain 22·26 per cent of soda, 12·20 alumina, 13·00 water, and 52·10 hypothetically anhydrous oxalic acid. (Bussy.)

Oxalate of Alumina and Baryta. — $3(BaO,C^2O^3)+(Al^2O^3,3C^2O^3)+10Aq.$ and $+30Aq.$ [$=C^{12}Ba^3Al^2O^{24}+10$ and $+30Aq.$] Separates on mixing a concentrated solution of chloride of barium with acid oxalate of alumina, in small, snow-white, silky needles, scarcely dissolving in cold water, but soluble in 30 pts. of boiling water. Ammonia separates the oxalic acid from the alumina. (Rees Reece, *Compt. rend.* 21, 111, 6.)

Oxalate of Alumina and Strontia. $3(SrO,C^2O^3)+(Al^2O^3,3C^2O^3)+18Aq.$ [$=C^{12}Sr^3Al^2O^{24}=18Aq.$] — Resembles the baryta-compound, but is decomposed by *boiling water.* (Rees Reece.)

The corresponding lime-salt could not be prepared, in consequence of its insolubility. (Reece.)

Oxalate of Thorina. — Oxalic acid forms with thorina-salts a heavy white precipitate, which, if washed with pure water not containing oxalic acid, runs milky through the filter. It is insoluble in water and oxalic acid, and dissolves very sparingly in other dilute acids. (Berzelius.)

Oxalate of Thorina and Potash. — White precipitate which turns black when ignited, and then, if in contact with the air, leaves a white mixture of thorina and carbonate of potash, which forms a milky liquid with water. Does not dissolve in water or in aqueous oxalic acid. (Berzelius.)

Oxalate of Zirconia. — Oxalic acid and oxalate of ammonia throw down white flakes from solutions of zirconia-salts. The precipitate, after drying, has the colour of opal. It is not soluble in water or in boiling aqueous oxalic acid. (Dubois & Silveira.)

Oxalate of Titanium. — Precipitated in the form of a curdy mass, on boiling an aqueous solution of a titanic salt mixed with oxalic acid. (Laugier.) — Any ferric oxide that may be contained in the liquid remains in it for the most part. — The dried precipitate imparts to moist litmus-paper a red tint, which nearly disappears on drying. The precipitate is soluble in excess, both of aqueous oxalic acid and of hydrochlorate of titanium. (H. Rose.)

				H. Rose.
13 TiO^2	520	....	74·29	..... 74·11
C^4O^6	72	....	10·29	..... 10·40
12 HO	108	....	15·42	..... 15·49
$12TiO^2,C^4TiO^8+12Aq$	700	....	100·00	..... 100·00

Oxalate of Tantalum. — According to Wollaston, oxalic acid dissolves recently precipitated hydrated tantalic acid; according to Gahn, Berzelius, and Eggertz, oxalic acid dissolves only a trace, but salt of sorrel at a boiling heat dissolves a considerable quantity, forming a colourless solution, from which alkalis throw down the tantalic acid. If the solution in salt of sorrel also contains tungstic acid, and is saturated while hot, it solidifies on cooling, in a milk-white jelly, and becomes tinged with blue when a piece of tin or zinc is immersed in it. (Berzelius.)

Molybdous Oxalate. — Dark grey precipitate, which turns black when dried, and is sparingly soluble in excess of oxalic acid. (Berzelius, *Pogg.* 6, 379.)

Molybdic Oxalate. — Crystallizes in blackish blue crystals when the aqueous solution is left to evaporate spontaneously. From its solution in water, which is red, ammonia throws down a pale brick-red, *basic salt* insoluble in excess of ammonia. (Berzelius, *Pogg.* 6, 348.)

Oxalate of Blue Oxide of Molybdenum. — Blue solution, which leaves a blue mass when evaporated, becomes green when diluted with a small quantity of water, but brown on being mixed with a large quantity. (Heyer, *Crell. Ann.* 1784, 2, 14.)

Oxalate of Molybdic Acid. — Formed by digesting molybdic acid with aqueous oxalic acid. The solution, which is colourless even when the molybdic acid is in excess, yields on evaporation a colourless jelly, which becomes crystalline without further dessication, dissolves in water, and with yellow colour in alcohol. (Berzelius, *Pogg.* 6, 384.)

Oxalate of Molybdous Oxide and Potash. — Purple; soluble in water. (Berzelius.)

Oxalate of Molybdic Oxide and Potash. — Formed by dissolving the hydrated oxide in salt of sorrel. Soluble in water. (Berzelius.)

Oxalate of Molybdic Acid and Potash. — The aqueous solution of salt of sorrel readily dissolves molybdic acid, forming a non-crystallizable double salt. (Berzelius.)

Oxalate of Vanadic Oxide. — Aqueous oxalic acid saturated with hydrated vanadic oxide, yields on evaporation a light blue, translucent gum, which dissolves slowly in cold water, more quickly in hot water. The aqueous solution mixed with a large quantity of oxalic acid, yields by spontaneous evaporation, blue crystals readily soluble in water. (Berzelius, *Pogg.* 22, 33.)

Oxalate of Vanadic Acid. — When oxalate of vanadic oxide is evaporated with nitric acid, and the residue treated with water, the greater part dissolves, forming a yellowish red solution, which on evaporation leaves oxalate of vanadic acid in the form of a reddish yellow, amorphous extract, likewise soluble in water. An excess of oxalic acid immediately reduces the vanadic acid to vanadic oxide. (Berzelius, *Pogg.* 22, 42.)

Oxalate of Vanadic Oxide and Potash. — Salt of sorrel saturated with hydrated vanadic oxide, dries up to a dark blue, amorphous varnish, which dissolves slowly in water. (Berzelius.)

Oxalate of Chromic Oxide or *Chromic Oxalate.* — *a. Insoluble.* — Normal oxalate of ammonia forms with hydrochlorate of chromic oxide a pale green, pulverulent precipitate. (Hayes, *Sill. Am. J.* 14, 140.) — *b. Soluble.* — $Cr^2O^3,3C^2O^3=C^{12}Cr^4O^{24}$. The saturated solution of chromic oxide in aqueous oxalic acid, which is red by transmitted and green by reflected light, and does not redden litmus, leaves when evaporated, a green salt which becomes moist on exposure to the air, and dissolves readily in water. (Brandenburg, *Scher. Nord. Bl.* 1, 208, and 219.) — The solution, when prepared in the cold, has a cherry-red colour, but if prepared at a boiling heat, it is green, but assumes the cherry colour on cooling. When left to evaporate spontaneously, it dries up to a black vitreous mass, which splits up into small pieces, exhibiting a violet-red colour by light transmitted through their edges. But a solution which has been turned green by boiling, leaves a green mass when evaporated over the water-bath. (Berlin, *Berzelius Lehrb.*) — Brandenburg's statement that the salt is rendered crystalline by a larger addition of acid, is not confirmed by Berlin's observations, that which crystallizes out appearing to be merely the excess of oxalic acid. — The aqueous solution is not precipitated by alkalis, but unites with them, forming double salts. (Brandenburg.) — It does not precipitate lime-salts, because the oxalate of lime produced forms with the chromic oxalate a somewhat soluble double salt; but it precipitates chloride of lime, because that salt converts the chromic oxide into chromic acid, decomposing at the same time a portion of the oxalic acid. (Em. Dingler, *Kastn. Arch.* 18, 251.) — The solution is not precipitated by ammonia or by lime-salts; but it gives a precipitate with lime-water, and when heated, likewise with potash. (Berlin.)

Chromic oxalate forms with the oxalates of the alkalis and earths, two series of salts, viz. dark-blue salts which form bluish green solutions in water, and cherry-red or garnet-coloured salts forming cherry-red solutions in water. The formula of the *blue salts* is $3(\dot{M}O,C^2O^3)+Cr^2O^3,3C^2O^3=C^{12}M^3Cr^2O^{24}$ (Gm.) $=C^4MCr\beta O^8$ (Gerhardt); that of the red

salts is $MO,C^2O^3 + Cr^2O^3,3C^2O^3 = C^8MCr^2O^{16}$ (Gm.) — The potash-salt of the blue series was discovered by Turner and Gregory; the potash-salt of the red series by Croft.

Blue Ammonio-chromic Oxalate.—The crystals contain $3(NH^4O,C^2O^3) + Cr^2O^3,3C^2O^3 + 6$ Aq. (Mitscherlich), or 5 Aq. (Berlin) $= C^{12}(3NH^4,Cr^2)O^{24} + 6$ or 5 Aq. — Obtained by saturating acid oxalate of ammonia dissolved in water with hydrated chromic oxide. (Mitscherlich, *Lehrb.*) The aqueous solution when evaporated yields scales and laminæ containing 10·72 per cent of water, which they give off at 100°, assuming a light blue colour, and then, when more strongly heated, leave chromic oxide in the form of laminæ. They dissolve in $1\frac{1}{3}$ pt. water at 15°, and in a smaller quantity of hot water. (Berlin, *Berzelius Lehrb.*)

Red Ammonio-chromic Oxalate.—In the crystalline form $= NH^4O,C^2O^3 + Cr^2O^3,3C^2O^3 + 8$ Aq. $= C^8(NH^4,Cr^2)O^{16} + 8$Aq. — The crystals resemble those of the red potash-salt, in colour, general appearance, and solubility, but are often more shining, and are transparent and garnet-coloured. They contain 24·89 per cent of water and effloresce when heated, assuming a light red colour. (Berlin.)

Blue Potassio-chromic Oxalate. — The composition of the hydrated crystals is $3(KO,C^2O^3) + Cr^2O^3,3C^2O^3 + 6$Aq. (Graham, Mitscherlich, Berlin); $= C^{12}K^3Cr^2O^{24} + 6$Aq.*

Preparation. 1. An aqueous solution of acid oxalate of potash is saturated at a boiling heat with hydrated chromic oxide (Malaguti, *Compt. rend.* 16, 458; Warington, *Phil. Mag. J.* 21, 202; Berlin.):

$$3C^4HKO^8 + Cr^2O^3 = C^{12}K^3Cr^2O^{24} + 3HO.$$

Croft did not succeed in preparing the blue salt by this process. — 2. Bichromate of potash is boiled with oxalic acid and acid (or normal) oxalate of potash, whereupon carbonic acid is evolved, and the chromic acid reduced to chromic oxide (Gregory): — Equation for acid oxalate of potash:

$$2(KO,2CrO^3) + 4C^4HKO^8 + 5C^4H^2O^8 = 12CO^2 + 14HO + 2C^{12}K^3Cr^2O^{24}.$$

Equation for normal oxalate of potash:

$$2(KO,2CrO^3) + 2C^4K^2O^8 + 7C^4H^2O = 12CO^2 + 14HO + 2C^{12}K^3Cr^2O^{24}.$$

According to this calculation, Croft (*Phil. Mag. J.* 21, 197; also *J. pr. Chem.* 27, 431) uses 19 pts. of bichromate of potash, 23 pts. of crystallized normal oxalate of potash, and 55 pts. of hydrated crystallized oxalic acid. [The exact stoïchiometric proportion is 151·2 : 184 : 441.] — The mixture is boiled with water and evaporated to complete dryness, the residue redissolved in water, and the solution left to crystallize; by this process nothing but the blue salt is obtained. (Croft.) — Berlin uses the same relative quantities of material, excepting that he takes 27 parts of oxalate of potash, instead of 23 (which is probably a misprint, inasmuch as it should be 2 At.). He adds the oxalic acid in successive small portions to the boiling solution of the chromate of potash, and then, as soon as the evolution of carbonic acid ceases, the normal oxalate of potash; afterwards evaporates and cools the solution; and purifies the resulting crystals by recrystallization. — [When acid oxalate of potash is used, the proportions are: 151·2 pts. of bichromate of potash, 292·4 pts. of acid oxalate, and

* The two formulæ according to the substitution-theory given on page 210, line 4. vol. VII, are inadmissible.

315 pts. of hydrated oxalic acid.] — Gregory recommended 190 pts. (1 At.) of bichromate of potash, 517 pts. (not quite 3 At.) of acid oxalate of potash, and 151·5 pts (1 At.) of crystallized oxalic acid; but, according to Croft, these quantities yield crystals of chromate and oxalate of potash as well as of the blue salt. — Graham takes 1 pt. of bichromate of potash, 1 pt. of acid oxalate of potash, and 1 pt. of hydrated oxalic acid; but, according to Croft, these proportions leave a large quantity of chromate of potash undecomposed. — 3. The aqueous solution of 86 pts. (1 At.) carbonate of potash and 245 pts. (2 At.) monochromate of potash is heated with 632 pts. (4 At.) of hydrated oxalic acid. Carbonic acid is then evolved, and a dark green solution formed, which yields crystals on cooling. (Bussy.) These proportions nearly correspond with the equation:

$$KO,CO^2 + 2(KO,CrO^3) + 4C^4H^2O^8 = C^{12}K^3Cr^2O^{24} + 5CO^2 + 8HO + O.$$

The 1 At. O thus set free probably decomposes a small quantity of oxalic acid. — Turner, whose memoir I have not seen, appears to have heated an aqueous solution of bichromate of potash with oxalic acid, a process which, according to Croft, yields not the blue but the red salt.

Properties. The anhydrous salt, which is obtained by dissolving the hydrated salt in a hot concentrated solution of the corresponding soda-salt, and cooling the mixture, crystallizes in octohedrons, containing but a small quantity of the soda-salt. (Mitscherlich.)

The hydrated salt forms large rhombic prisms (Gregory, Bussy), with dihedral summits, and having the two acute lateral edges truncated. (Berlin.) The crystals are black and lustrous by reflected light, but by transmitted light they exhibit a blue colour resembling that of the corn-flower. (Gregory; see also Haidinger, *Pogg.* 76, 107.) The powder is greenish. (Bussy, Berlin.) The crystals intercept the middle portion of the red rays of the spectrum. (Brewster.)

	Anhydrous.		
3 KO	141·6	.....	32·36
Cr^2O^3	80·0	.....	18·28
3 C^4O^6	216·0	.....	49·36
$C^{12}K^3Cr^2O^{24}$	437·6	.....	100·00

With Water of Crystallization.			Graham.		Bussy.
3 KO	141·6	28·81			
Cr^2O^3	80·0	16·27	16·46		16·52
3 C^4O^6	216·0	43·94	44·17		44·31
6 HO	54·0	10·98	11·67		10·60
$C^{12}K^3Cr^2O^{24} + 6Aq$	491·6	100·00			

The crystals when heated to 100°, give off 9·15 per cent of water, according to Berlin, but 10·6 p. c. according to Bussy; when dried at a higher temperature, they give off 11·6 per cent. (Graham.) The residue is a dark green powder. (Berlin.) At a red heat, it gives off carbonic acid, and leaves a mixture of carbonate and chromate of potash, amounting to 54·37 per cent, and perfectly soluble in water. (Graham.) — The salt dissolves in 5 pts. of water at 15°. (Berlin.) The solution is green by reflected, red by transmitted light. (Gregory, Bussy.) According to Croft, it remains red by transmitted light when boiled; but according to Berlin, the chromic oxide passes at a boiling heat from the violet modi-

fication into the green; and the boiled solution, if evaporated by heat, yields a green, amorphous residue which becomes fissured in drying, but by solution in water and spontaneous evaporation again yields the blue crystals. (Berlin.) Alkalis added to the solution throw down only a portion of the chromic oxide (Gregory); so likewise does carbonate of potash (Graham); ammonia gives no precipitate; potash, only at a boiling heat. (Berlin.) Lime-salts form but a scanty precipitate (Gregory; none, unless the solution is highly concentrated (Reece); but baryta-water and lime-water throw down a mixture of hydrated chromic oxide and oxalate of baryta or lime. (Berlin.) Alcohol does not dissolve the salt, but throws it down from the aqueous solution in the form of a green powder. (Berlin.)

Red Potassio-chromic Oxalate. — The crystals contain: $KO,C^2O^3 + Cr^2O^3, 3C^2O^3 + 8Aq. = C^8KCr^2O^{16} + 8Aq.$ — The salt is obtained by gradually adding 55 pts. [or 882 pts. = 7 At.] hydrated oxalic acid to a boiling concentrated solution of 19 pts. [or 302·4 pts. = 2 At.] of bichromate of potash. (Croft. *Phil. Mag. J.* 21, 197.)

$$2(KO,2CrO^3) + 7C^4H^2O^8 = 12CO^2 + 14HO + 2C^8KCr^2O^{16}.$$

Better crystals are obtained by spontaneous evaporation than by cooling. (Croft.) — The salt is also formed by saturating an aqueous solution of hyperacid oxalate of potash with hydrated chromic oxide. (Malaguti, *Compt. rend.* 16, 456; also *J. pr. Chem.* 29, 294.)

$$Cr^2O^3 + C^8H^2KO^{16} = C^8KCr^2O^{16} + 3HO.$$

Also by saturating an aqueous solution of 126 pts. (1 At.) of hydrated oxalic acid and 146·2 pts. (1 At.) of salt of sorrel with hydrated chromic oxide. (Warington.)

Very small tables and granules. (Croft.) Spangles and crusts composed of slender needles. (Berlin.) Rhombic or rhomboidal tables, somewhat like *Fig.* 114. (Miller, *Phil. Mag. J.* 21, 201.) Dark red both by reflected and by transmitted light. (Croft.)

	Crystallized.			Croft.	Berlin.
KO	47·2	....	12·45	12·86	
Cr^2O^3	80·0	....	21·09	22·33	
2 C^4O^6	144·0	....	37·98	38·29	
12 HO	108·0	....	28·48	26·97	28·46
$C^8KCr^2O^{16} + 12Aq$	379·2	....	100·00	100·45	

According to Malaguti, the crystals contain only 8 At. water, but according to Löwel (*Compt. rend.* 18, 862) they contain at least 10 At.

The crystals give off 15 or 16 per cent of water at 100°, and 19 p. c. at 200°. (Croft.) They give off nothing at 50°, but at 100° they part with the half of their water, becoming at the same time light red and opaque. (Berlin.) The residue, when suddenly heated, is converted into a green powder, part of which is thrown out of the vessel by the violence of the decomposition. The crystals, if subjected to a very slowly increasing heat, retain their form at first and assume a dark green colour, but afterwards crumble to a light green powder of chromic oxide, which turns brown when more strongly heated, and is mixed with carbonate, or after continued ignition in the air, with chromate of potash. (Croft.)

The salt dissolves in somewhat more than 10 pts. of cold water, and in any quantity of boiling water; the boiling solution is blackish green; the cold solution, cherry-red; the boiled solution, when left to cool

deposits in a few days a number of garnet-coloured crystalline grains, but if evaporated immediately over the water-bath, yields a green amorphous mass. (Berlin.) — The concentrated solution is dark green and even black by reflected light, but red by transmitted light, even after continued boiling, and especially by candlelight. Potash changes the colour of the solution to a splendid green, but does not precipitate the chromic oxide till boiled; carbonate of potash acts in a similar manner, but does not so readily produce a precipitate. Ammonia gives no precipitate; chloride of calcium likewise forms no precipitate alone; but with addition of ammonia, it throws down a green precipitate. (Croft.) Alcohol added to the aqueous solution of the salt throws down a light red powder, which, after drying, absorbs water from the air, and deliquesces to a transparent, garnet-coloured mass. (Berlin.) 237 pts. (1 At.) of this salt and 115 pts. (1 At.) of crystallized normal oxalate of potash, dissolved in boiling water, yield by evaporation 311·9 pts. [somewhat more than 1 At.] of crystallized blue potassio-chromic oxalate. (Croft.)

Blue Sodio-chromic Oxalate. — $3(NaO,C^2O^3) + Cr^2O^3,3C^2O^3 + 9Aq.$ [$= C^{12}Na^3Cr^2O^{24} + 9Aq$] (Mitscherlich); +10 Aq. (Graham.) Obtained by saturating a boiling aqueous solution of acid oxalate of soda with hydrated oxide of chromium. (Mitscherlich.) — Six-sided tables or rhombic prisms, black by reflected, dark blue by transmitted light; efflorescing slightly in the air, and assuming a violet colour. The salt dissolves readily in water, and is precipitated therefrom by alcohol as a greenish blue syrup. (Berlin.)

The aqueous solution of this salt mixed with that of normal oxalate of soda, yields by spontaneous evaporation, violet-blue scales and granules which become violet-red by efflorescence on exposure to the air, and contain $2(NaO,C^2O^3) + Cr^2O^3,3C^2O^3 + xAq$. (Berlin. *Berzelius, Lehrb.* 3, 1089.) [It is not easy to understand how oxalate of soda can abstract an atom of oxalate of soda from the blue salt just described.]

¶ According to Rammelsberg (*Pogg.* 93, 51), a solution of hydrated chromic oxide in binoxalate of soda yields two salts, agreeing in composition, but differing in form and colour.

a. Red Salt. — This salt crystallizes out first. The crystals are black, but when reduced to thin laminæ, exhibit a violet-red colour by transmitted light; they also yield a reddish-grey powder. They belong to the hemihedral division of the regular system. Their solution is violet-red, is not precipitated by ammonia, but gives a coloured precipitate after a while with chloride of calcium.

b. Blue Salt. — Found mixed with *a* in the later crops of crystals. Black by reflected, but blue in thin laminæ by transmitted light. Crystallizes generally in octagonal tables isomorphous with sodio-ferric oxalate. The powder and the aqueous solution of this salt have the same colour as those of *a*; it likewise gives the same reactions with ammonia and with lime-salts:

	Crystallized.			Rammelsberg. *Red.*		*Blue.*
3 NaO	93·6	....	19·89	20·56	....	19·89
Cr^2O^3	80·0	....	17·00	16·78	....	16·89
3 C^4O^3	216·0	....	45·90			
9 HO	81·0	....	17·21			
$C^{12}Na^3Cr^2O^{24} + 9Aq$	470·6	....	100·00			

$= 3(NaO,C^2O^3) + (Cr^2O^3,3C^2O^3) + 9Aq$. ¶

Baryta-chromic Oxalate. — $3(BaO,C^2O^3) + (Cr^2O^3,3C^2O^3) + 12Aq.$ and 18Aq. [$=C^{12}Ba^3Cr^2O^{24}+12Aq.$ and 18Aq]. Baryta-salts yield with acid chromic oxalate, and with blue ammonio-chromic or potassio-chromic oxalate, but only when the solutions are highly concentrated, a precipitate consisting, not of oxalate of baryta, but of baryto-chromic oxalate. The salt is obtained by precipitating a saturated solution of blue ammonio-chromic oxalate, with an equal volume of a saturated solution of chloride of barium, separating the precipitate from the mother-liquid, and purifying it by crystallization from a hot aqueous solution. — Dark-violet needles having a silky lustre. They are scarcely soluble in cold water, but dissolve in 30 pts. of boiling water. Potash separates the chromic oxide together with oxalate of baryta, but ammonia does not precipitate the chromic oxide completely. (Rees Reece). — Berlin had previously obtained light blue crystals, probably of the same nature, by dissolving oxalate of baryta in chromic oxalate, and cooling the solution.

Strontio-chromic Oxalate. — $3(SrO,C^2O^3) + Cr^2O^3,3C^2O^3 + 18Aq.$ [$= C^{12}Sr^3Cr^2O^{24} + 18Aq.$] — Analogous in all respects to the baryta-salt. (Rees Reece.)

Calcio-chromic Oxalate. — *a.* $3(CaO,C^2O^3) + Cr^2O^3,3C^2O^3 + 18Aq.$ (Berlin.) [$= C^{12}Ca^3Cr^2O^{24} + 18Aq.$] According to Berlin, the salt contains 33·84 per cent of water, which corresponds to at least 20 atoms. — 1. It is obtained by boiling a concentrated solution of chromic oxalate with recently precipitated oxalate of lime, throwing on a filter the violet magma which settles down from the hot filtrate as it cools, and washing it; it is then converted, by the removal of the blue mother-liquor, into shining rose-coloured, crystalline laminæ, which dry up to a rose-coloured crust. — 2. A boiling aqueous solution of chromate of lime is reduced by oxalic acid; in this case also, the liquid filtered hot from the precipitated oxalate of lime, deposits a magma which must be treated as in the former process. (Berlin.) The salt, when heated to 100°, gives off only 23·81 per cent of water, assuming a light blue colour. — It dissolves in not less than 200 parts of cold water, and in a much smaller quantity of boiling water; but the hot solution deposits nothing on cooling, till it is evaporated to a syrupy consistence. If however the solution be evaporated over the water-bath, there remains an amorphous mass of the green modification, which dissolves in a very small quantity of water, and then again deposits the red salt of the violet modification. The salt, when boiled with a large quantity of water, is partly resolved into oxalate of lime, which separates, and free chromic oxalate; the liquid filtered from the oxalate of lime and left to evaporate spontaneously, deposits the undecomposed red double salt, while the excess of acid chromic oxalate remains in the mother-liquor. The cooled filtrate mixed with alcohol, which retains the excess of chromic oxalate in solution, likewise deposits a dark-red magma of the undecomposed red salt, deliquescing in the air to a dark-brown syrup, from which the rose-coloured powder is soon deposited. (Berlin.)

b. $3(CaO,C^2O^3) + Cr^2O^3,3C^2O^3 + 36Aq.$ — Dark violet silky needles, exhibiting all the characters ascribed by Reece to the corresponding baryta-salt, excepting that they are decomposed by boiling water. (Reece.)

The formation of this somewhat soluble salt explains the observation made by Dingler (*Kastn. Arch.* 18, 251), that from liquids containing lime and chromic oxide, the lime is not completely precipitated by oxalic acid; if however, such a liquid containing excess of hydrochloric acid, be

treated with oxalic acid and then with oxalate of ammonia in excess, the lime will be completely precipitated. Similar reactions take place when, instead of chromic oxide, alumina or ferric oxide—both of which form similar salts with lime and oxalic acid—is present in an acid solution, together with lime. (Rees Reece.)

Magnesio-chromic Oxalate. — An aqueous mixture of chromic oxalate with chromate of magnesia leaves by spontaneous evaporation a mixture of blue and red crystals which are difficult to separate. (Berlin.)

Uranous Oxalate. — Obtained by precipitating protochloride of uranium with oxalic acid, and washing the precipitate repeatedly with boiling water to separate any uranic oxalate that may be mixed with it, in consequence of the protochloride of uranium having been oxidized by exposure to the air. — Greenish white; may be dried in the air and preserved without decomposition. Of its 6 At. water it gives off 4 At. in vacuo. (Péligot, *N. Ann. Chim. Phys.* 5, 26 and 32.) — Rammelsberg, (*Pogg.* 59, 20) by the same process, excepting that he does not appear to have washed with hot water, obtained a greyish-green powder, which gave off 12·83 per cent of water at 100°, 13·14 per cent at 220°, and 17·30 per cent at the highest temperature which it could bear without decomposition; when subjected to dry distillation, it was resolved into water, oxalic acid, carbonic oxide, carbonic acid, and uranoso-uranic oxide; it was readily and completely decomposed by aqueous ammonia and potash, and dissolved with difficulty in hydrochloric acid.

			Péligot.	Rammelsberg.
2 UO	136	51·91	50·6	54·31
C^4O^6	72	27·48	27·6*	27·56
6 HO	54	20·61	20·7	17·30
$C^4U^2O^8 + 6Aq$	262	100·00	98.9	99·17

* Inasmuch as Péligot found 9·2 per cent. of carbon. The salt analyzed by Rammelsberg had been dried over oil of vitriol, and thereby perhaps deprived of part of its water.

When the salt is boiled with aqueous oxalic acid, it is converted, without loss, into a salt, which, according to Rammelsberg, contains 52·10 per cent uranous oxide, 41·12 oxalic acid, and therefore 6·78 water; he regards it as $UO,C^2O^3 + UO,2C^2O^3 + 2Aq$. It is a question however whether this salt was not contaminated with uranic salt. When a small quantity of recently precipitated hydrate of uranous oxide is introduced into aqueous oxalic acid, a green solution is obtained; but when a larger quantity of the hydrate is added, the product just mentioned is precipitated. (Rammelsberg.)

Uranic Oxalate. *a. Basic?* — Berzelius (*Pogg.* 1, 362 and 368), in attempting to purify uranic oxalate by dissolving it in aqueous carbonate of ammonia, and precipitating from the filtrate by continued boiling, obtained, on one occasion, this salt, on another, the following salt *b*. He however considered it probable that the salt *a* thus obtained might be contaminated with ammonia, and therefore did not place implicit confidence in the analysis.

Well dried.			Berzelius.
$3\ U^2O^3$	432	78·69	79·63
C^4O^6	72	13·11	12·45
5 HO	45	8.20	7·92
$U^2O^3 + C^4(2U^2O^2)O^8 + 5Aq$	549	100·00	100·00

b. Normal. — 1. Formed by precipitating uranic nitrate with concentrated oxalic acid. (Berzelius.) — Berzelius purified the salt by solution in

carbonate of ammonia, &c. *vid. Salt a.* — If the solutions be mixed cold, the salt is precipitated in the form of a powder, but when they are mixed hot, it separates on cooling in yellow crystalline grains. (Péligot). — When the solutions mixed are hot and concentrated, a viscid magma is first formed, which gradually changes to a yellow crystalline powder; this is washed with water, till the liquid which runs through gives but a slight reddening with litmus, arising from the portion of uranic oxalate which dissolves. The salt may also be purified by dissolving it in boiling water; but the method is troublesome, because the salt is but very slightly soluble even in hot water. (Ebelmen.) — 2. By precipitating a uranic salt with oxalate of potash. (Richter, *Neuere Gegenst.* 1, 16.)

The salt obtained by the first process consists of a sulphur-coloured powder or crystalline grains, which, according to Ebelmen, have a density of 2·98. The second process yields a yellowish white powder. (Richter.)

	Dried at 100°.			Ebelmen.
$2\,U^2O^3$	288	76·19		76·29
C^4O^6	72	19·05		18·73
2 HO	18	4·76		4·98
$C^4(2U^2O^2)O^8 + 2Aq$	378	100·00		100·00

	Air-dried.		Berzelius.		Péligot.	
$2\,U^2O^3$	288	69·57	69·00		69·78	
C^4O^6	72	17·39	17·99		17·70*	
6 HO	54	13·04	13·01		13·70	
$C^4(2U^2O^2)O^8 + 6Aq$	414	100·00	100·00		101·18	

* Péligot found 5·90 p.c. carbon.

The air-dried salt heated to 100°—120°, gives off nearly 9 per cent of water, which it takes up again from the air; at 300°, it turns brown, and is converted almost instantly, with evolution of water and carbonic acid, into a copper-coloured powder of uranous oxide, which by ignition in the air, is converted into green uranoso-uranic oxide (Ebelmen):

$$C^4(2U^2O^2)O^8 + 2Aq = 4UO + 4CO^2 + 2Aq.$$

The same result had been previously obtained by Berzelius, excepting that he regarded the uranous oxide as metallic uranium. — The aqueous solution exposed to the sun continually gives off carbonic oxide and carbonic acid gases in varying relative quantity; becomes turbid; and deposits violet-brown flakes of uranoso-uranic oxide, till all the oxalic acid is destroyed and liquid is decolorized: the precipitated uranoso-uranic hydrate gradually assumes a yellow colour, and if exposed to the air becomes perfectly yellow by conversion into uranic hydrate. (Ebelmen.) — The salt dissolves in 125 pts. of water at 14° and in 30 pts. of boiling water; it dissolves somewhat more readily in the stronger acids, and easily in warm aqueous oxalate of ammonia or potash, with formation of double salts which crystallize on cooling. (Ebelmen.) An excess of aqueous oxalic acid dissolves uranic hydrate even in the cold. The yellow solution, which scarcely reddens litmus, yields on evaporation, indistinctly crystalline crusts, and when evaporated out of contact of air, yields uranium [uranous oxide] in the form of a powder destitute of lustre. (Trommsdorff, *N. Tr.* 9, 1, 286.)

Ammonio-uranous Oxalatue. — The dark green solution, reddish on the edges, of recently precipitated uranous hydrate in hot acid oxalate of ammonia, yields by evaporation, crystals which must be freed as com-

pletely as possible from admixed oxalate of ammonia by recrystallization (Rammelsberg):

	Crystals dried over oil of vitriol.			Rammelsberg.
NH^3	17	....	10·24	..... 11·02
UO	68	....	40·96	..... 37·65
C^4O^6	72	....	43·38	..... 39·44
HO	9	....	5·42	
$C^4(NH^4,U)O^8$	166	....	100·00	

Ammonio-uranic Oxalate. — Uranic oxalate dissolves abundantly in warm aqueous ammonia, and yields beautiful yellow transparent prisms when the solution is evaporated, (Péligot, *N. Ann. Chim. Phys.* 5, 49). Twelve-sided prisms belonging to the right prismatic system, with dihedral summits. *Fig.* 75, together with the *t*-face, by which the lateral edge between *n* and *n* behind is truncated. $y : x$ backwards $= 112° 25'$; $y : a = 115° 15' : y : n = 106° 30'$; $m : u = 139° 55' u : n = 160° 45'$. (Prevostaye, *ibid.*)

	Crystallized.			Péligot.
NH^3	17	....	6·11	
U^2O^3	144	....	51·80	..... 52·6
C^4O^6	72	....	25·90	..... 25·8
5 HO	45	....	16·19	
$C^4(NH^4,U^2O^2)O^8+4Aq$	278	....	100·00	

Péligot found in the salt, 8·6 p.c. carbon and 2·5H; he supposes it to contain only 3 At. water.

Potassio-uranous Oxalate. — Recently precipitated uranous hydrate boiled with an aqueous solution of salt of sorrel, is coverted into a grey powder, only a very small quantity remaining in solution with a green colour. The powder, heated in a retort, after having been dried over oil of vitriol, becomes first brown, then black; gives off 13·08 per cent of water; and leaves a mixture of uranous oxide and carbonate of potash, containing 49·60 per cent of the salt as uranous oxide and 7·10 as potash, according to which numbers the salt should be $= KO + UO + 6C^2O^3 + 10Aq$. (Rammelsberg, *Pogg.* 59, 20.)

Potassio-uranic Oxalate. — Obtained by saturating a hot aqueous solution of normal oxalate of potash with uranic oxalate, filtering hot, and leaving the solution to crystallize by cooling. — Large, lemon-yellow oblique rhombic prisms, transparent and permanent in the air. *Fig.* 114, $u' : u = 131° 2'$; $u' : t = 144° 20'$; u' or $u : m = 111° 28'$; $a : m = 140° 52'$; $a : u = 150° 36'$. Effloresces and gives off all its water at 100°, and is converted at 300° into a black mixture of uranous oxide and carbonate of potash; or if the air has access to it, into a yellowish red mixture of carbonate and uranate of potash. The aqueous solution is not decomposed by exposure to sunshine. Chloride of calcium does not throw down all the oxalic acid from it, and the precipitated oxalate of lime contains also uranate of lime. (Ebelmen, *N. Ann. Chim. Phys.* 5, 189; also *Ann. Pharm.* 43, 269.)

	Crystallized.			Ebelmen.
KO	47·2	....	16·26	..... 15·86
U^2O^3	144·0	....	49·62	..... 49·92
C^4O^6	72·0	....	24·81	..... 24·73
3 HO	27·0	....	9·31	..... 9·35
$C^4(K,U^2O^2)O^8+3Aq$	290·2	....	100·00	..... 99·86

When uranic oxalate is dissolved in excess of an aqueous solution of normal oxalate of potash, and the hot filtrate evaporated, nearly all the double salt is deposited, and may be purified by recrystallization. It takes the form of small aggregated crystals resembling those of gypsum, and quickly giving off their water a little above 100°; their aqueous solution is decomposed by sunshine. These crystals contain 19·70 per cent KO, 40·50 U^2O^3, 25·63 C^4O^6, and 13·09 Aq. (the sum of which is 98·92); their formula is therefore $3(KO,C^2O^3)+2(U^2O^3,C^2O^3)+10Aq$. (Ebelmen.)

Manganous Oxalate. — Manganous carbonate forms with aqueous oxalic acid a liquid from which the salt is deposited in the form of a white crystalline powder. (Bergman; Hausmann and Löwenthal.) The same salt is quickly produced on mixing a not too dilute solution of a manganous salt with oxalic acid (Bergman), or with oxalate of potash or ammonia. (Bucholz, *N. Gehl.* 9; 676.) Excess of oxalate of potash prevents the precipitation, by forming a double salt. (Winckelblech.) — The compound is likewise formed, with evolution of carbonic acid, on treating manganoso-manganic oxide or peroxide of manganese with aqueous oxalic acid. (Bergman, Döbereiner.)

The white crystalline powder exhibits a reddish tint when dry. (Berzelius, *Lehrb.*) When the salt is precipitated by oxalate of potash from manganous sulphate dissolved in 100 pts of water, it separates in needles after a few days. The salt contains 24·16 per cent [5 At.] of water, no portion of which is given off at 100°. (Graham.) At a red heat, it gives off water, carbonic oxide, and carbonic acid gas, and leaves the green protoxide. (Trommsdorff, *N. Tr.* 9, 1, 286; Bachmann.) It is completely decomposed by hot nitric acid. (Dujardin, *J. pr. Chem.* 15, 309.) Aqueous ammonia precipitates part of the manganous oxide, and forms a solution, which besides ammonia and oxalic acid, still contains manganous oxide, and when evaporated to dryness, deposits that substance but partially in the form of manganic oxide, so that on treating the residue with water, the greater part of the manganous oxide is redissolved. (Winckelblech, *Ann. Pharm.* 13, 280.) The salt dissolves in 900 pts. of cold, and in a smaller quantity of boiling water; cold aqueous oxalic acid (1 acid to 10 water) does not dissolve it much more abundantly than water, but hot aqueous oxalic acid dissolves it in much larger quantity. (Winckelblech, *Ann. Pharm.* 13, 280.) It is likewise not very soluble in dilute acetic acid. With aqueous sulphate, nitrate, hydrochlorate, or succinate of ammonia, it forms at ordinary temperatures a turbid solution, which, however, becomes clear when heated. (Wittstein, *Repert.* 57, 32.)

	Dried at 100°.		Hausmann & Löwenthal.
2 MnO	72	40	39·92
C^4O^6	72	40	39·20
4 HO	36	20	20·88
$C^4Mn^2O^8+4Aq$	180	100	100·00

Manganic Oxalate. — Brown manganic oxide forms with cold concentrated oxalic acid, a brown solution, which, when mixed with potash, assumes a reddish purple colour from formation of permanganate of potash. (Fromherz, *Schw.* 44, 339.) — Manganese ores of loose structure form with aqueous oxalic acid, a purple solution, which is resolved, slowly

in the cold, but immediately on the application of heat, into carbonic acid and manganous oxalate. The quantity of manganous salt thus precipitated is much above that which corresponds to the quantity of carbonic acid evolved; for a portion of manganous salt was likewise held in solution through the medium of the manganic salt. (Berthier, *Ann. Chim. Phys.* 51, 88.)

Ammonio-manganous Oxalate.—Manganous oxalate dissolves readily in an aqueous normal oxalate of ammonia, forming a double salt which crystallizes in small white needles, effloresces to a yellow powder on exposure to the air, and dissolves sparingly in water. (Winckelblech.)

	Crystallized.			Winckelblech.
NH^3	17	10·00		10·36
MnO	36	21·18		20·36
C^4O^6	72	42·35		42·24
5 HO	45	26·47		27·16
$C^4(NH^4,Mn)O^8 + 4Aq$	170	100·00		100·12

Winckelblech supposes the salt to contain 1 At. less of water.

On mixing a not too dilute solution of the salt with ammonia, a *basic salt* separates in needles, or if the solution be somewhat stronger, in the form of a crystalline powder. (Winckelblech.)

			Winckelblech.
3 NH^3	51	13·28	13·34
3 MnO	108	28·13	27·64
2 C^4O^6	144	37·50	37·28
9 HO	81	21·09	20·98
$2NH^3 + C^4(NH^4,Mn)O^8 + C^4Mn^2O^8 + 8Aq$?	384	100·00	99·24

Potassio-manganous Oxalate.—The solution of manganous oxalate in aqueous normal oxalate of potash, yields faint rose-coloured crystals, which leave when ignited a mixture of manganous oxide and carbonate of potash; they are insoluble in water, but dissolve in aqueous oxalate of potash. (Winckelblech, *Ann. Pharm.* 13, 280.)

Potassio-manganic Oxalate?—A cold aqueous solution of salt of sorrel agitated with pulverized peroxide of manganese, gives off carbonic acid and forms a purple liquid. (Van Mons, *J. Pharm.* 5, 307.)

Oxalate of Arsenious Acid?—Warm aqueous oxalic acid scarcely acts on metallic arsenic, but readily dissolves arsenious acid. The solution when evaporated, yields prisms which, when fused at a gentle heat, give up part of their oxalic acid and yield beautiful vegetations; these have an acid reaction, sublime unaltered at a gentle heat, and at a stronger heat yield, first oxalic acid and afterwards arsenic. They dissolve readily in water and alcohol. (Bergman.)

Antimonic Oxalate.—Aqueous oxalic acid dissolves a small quantity of antimonic oxide prepared at a red heat, and leaves on evaporation crystalline grains which dissolve sparingly in water. The same compound is likewise formed by the action of oxalic acid on antimonic sulphate or acetate; whereas butter of antimony is not acted upon by oxalic acid. (Bergman.)—When antimonic oxide, precipitated by carbonate of ammonia from butter of antimony,—or powder of alga-

roth, — is boiled with oxalic acid, or when hydrochloric or tartaric acid is poured into the hot aqueous solution of potassio-antimonic oxalate, the same antimonic oxalate is likewise precipitated in the form of a white crystalline powder. It is insoluble in cold water, and is decomposed by hot water, which withdraws the acid from it. (Péligot, *N. Ann. Chim. Phys.* 20, 291.)

				Péligot.
SbO^3	153	....	65·38	..... 66·15
4 C	24	....	10·25	..... 10·43
6 O	48	....	20·51	
HO	9	....	3·86	..... 4·10
$C^4(H,SbO^2)O^8$	234	....	100·00	

¶ *Ammonio-antimonic Oxalate.* — A solution of binoxalate of ammonia boiled with excess of antimonic oxide, yields (together with the delicate prisms of the ammonia-salt), larger, transparent, shining crystals of the double salt. — [For the form *vid.* Rammelsberg, *Pogg.* 93, 64.] The salt gives off only a fraction per cent at 100°, and at 175° is already fused, blackened, and decomposed with loss of ammonia. Water decomposes it immediately, separating white antimonic oxide which does not redissolve on boiling. The filtrate, which still becomes slightly turbid when heated, forms with hydrochloric acid a copious crystalline precipitate, consisting essentially of quadroxalate of ammonia, but still retains a large quantity of antimony in solution. (Rammelsberg.)

	Crystallized.			Rammelsberg.
11 C^2O^3	396	....	46·59	..... 46·43
5 NH^4O	90	....	15·29	..... 15·45
2 SbO^3	306	....	36·00	..... 35·90
2 HO	18	....	2·12	..... 2·22
$5(NH^4O,C^2O^3) + 2(SbO^3,3C^2O^3) + 2Aq$	810	....	100·00	..... 100·00

This salt is analogous to the potash-salt *a* described below (p. 149); its rational formula is perhaps : $[3(NH^4O,C^2O^3) + (SbO^3,3C^2O^3)] + 2(NH^4O,C^2O^3) + (SbO^3,3C^2O^3) + 2Aq$. (Rammelsberg.) ¶

Potassio-antimonic Oxalate.—When 60 parts of salt of sorrel dissolved in water are boiled with 9 parts of antimonic oxide prepared in the humid way, only $6\frac{2}{3}$ pts. are dissolved. (Wenzel.) — 1. The salt is obtained by boiling equal parts of pulverized native sulphide of antimony and hyperacid oxalate of potash with water, leaving the filtrate to crystallize, and purifying it by recrystallization. (Lassaigne, *J. Chim. méd.* 3, 278; also *Mag. Pharm.* 19, 142.) — By boiling an aqueous solution of salt of sorrel with excess of antimonic oxide. (Bussy, *J. Pharm.* 24, 616.) — White needles, united in stellate groups, which redden litmus, have an astringent and afterwards an acid taste, and exert an emetic action, but not so powerful as that of tartar emetic. (Lassaigne.) Large, oblique four-sided prisms. (Bussy); transparent prisms. (Péligot, *N. Ann. Chim. Phys.* 20, 291.) They give off their water (9·5 per cent) at 100°; but a certain portion of the oxalic acid appears to volatilize at the same time. The aqueous solution diluted with water becomes turbid, and deposits antimonic oxide in the form a white powder, leaving salt of sorrel in solution together with undecomposed double salt. (Bussy.) The aqueous solution is decomposed with precipitation by mineral acids. The salt dissolves in 9·5 parts of water at 9°, and in a smaller quantity of hot water. (Lassaigne.)

Calculation of the crystals, according to Bussy.			Bussy.		Péligot.
3 KO	141·6	25·08			
SbO^3	153·0	27·10	27·33		24·80 to 26·2
12 C	72·0	12·75			13·70 „ 14·4
18 O	144·0	25·51			
6 HO	54·0	9·56	9·50		9·47 „ 12·0
	564·6	100·00			

According to Péligot, the formula is $3KO+SbO^3+7C^2O^3+6Aq$. — According to Lassaigne, the crystals contain 20·19 per cent of water. Possibly Lassaigne's salt was different from the above.

¶ According to Rammelsberg (*Pogg.* 93, 55), there exist three oxalates of antimony and potassium. When a solution of pure binoxalate of potash is boiled with antimonic oxide (prepared from algaroth-powder), as long as any of the oxide is dissolved, the filtrate yields on cooling an abundant crop of small crystals (*a*), an additional quantity of which are obtained by evaporation. Soon, however, larger crystals of another salt (*b*) show themselves, and together with them, crystals of the effloresing hydrate of oxalate of potash C^4HKO^8+Aq. (p. 126), also of the quadroxalate, $C^4HKO^8,C^4H^2O^8+4Aq$.; and sometimes also crystals of another double salt (*c*) more soluble than *a* or *b*.

a. This salt is formed even when the solution of binoxalate of potash is not completely saturated with antimonic oxide. The crystals, which are generally small and indistinct, belong to the oblique prismatic system. — [For the measurements of the angles of this and the following salts, see Rammelsberg's memoir.] — The salt is partially decomposed by water, with separation of antimonic oxide and formation of binoxalate of potash; but the greater part of the salt crystallizes again from the liquid, mixed at last wth crystals of *b*. The solution forms with hydrochloric acid a copious crystalline precipitate, containing a large quantity of quadroxalate of potash, and easily redissolving in excess of the acid :

	Crystallized.			Rammelsberg.
11 C^2O^3	396	39·57		40·0
5 KO	236	23·55		23·5
2 SbO^3	306	30·58		30·2
7 HO	63	6·30		6·3
$5(KO,C^2O^3)+2(SbO^3,3C^2O^3)+7Aq$	1001	100·00		100·0

According to this formula, the salt may be regarded as a compound of two other double salts, viz. $[3(KO,CO^2)+SbO^3,3C^2O^3)]+[2(KO,CO^2)+(SbO^3,3C^2O^3)]+7Aq$. — The former of these is identical with the salt *b*; the latter has not yet been isolated. Rammelsberg also proposes the simpler formula $3(KO,C^2O^3)+(SbO^3,3C^2O^3)+3Aq$. which, however, does not agree so well with the analysis, giving, in fact, 40·19 C^2O^3, 26·32 KO, 28·17 SbO^3, and 3·02 Aq.

b. The crystals of this salt are in general larger than those of *a*, and very lustrous and transparent; they belong to the right prismatic system. Heated to 100°, they give off 7·75 to 7·81 p.c. (nearly 5 At.) water; at 110°, the loss amounts to 10·85 p.c. (7 At.); and at 175°, the whole of the water = 13·00 p.c. (9 At.) is given off. At 250°, the salt blackens, decomposes, and if afterwards digested in water, leaves pulverulent antimony.

The salt dissolves completely in water. The clear, acid solution becomes turbid when heated, and does not recover its transparency on cooling. The precipitate consists essentially of antimonic oxide with

traces of oxalic acid and potash. Hydrochloric acid added in small quantity throws down antimonic oxalate; and after this precipitate has been separated, a further addition of acid produces a crystalline precipitate consisting chiefly of quadroxalate of potash. The solution of the salt precipitates baryta, lead and silver salts, the precipitates probably consisting of analogous double salts.

	Crystallized.		Rammelsberg.
6 C^2O^2	216·0	36·52	37·82
3 KO	141·6	23·91	24·12
SbO^3	153·0	25·88	25·40
9 HO	81·0	13·69	12·66
$3(KO,C^2O^3)+(SbO^3,3C^2O^3)+9Aq$	591·6	100·00	100·00

c. Sometimes obtained from the mother-liquor remaining after the separation of the two preceding salts; the crystals belong to the doubly oblique prismatic system. The salt forms a clear solution in water; hydrochloric acid precipitates it in the same manner as *a* and *b*.

	Crystallized.		Rammelsberg.
7 C^2O^3	252·0	47·07	45·43
2 KO	94·4	17·63	18·47
SbO^3	153·0	28·58	28·77
4 HO	36·0	6·72	7·33
$2(KO,2C^2O^3)+(SbO^3,3C^2O^3)+4Aq$	535·4	100·00	100·00

The composition of this salt must be considered as doubtful, as it was not constantly obtained. (Rammelsberg.) ¶

Telluric Oxalate. — Aqueous oxalic acid does not dissolve dry telluric oxide, but it dissolves the hydrate, and yields crystalline grains consisting of radii diverging from a centre; they dissolve readily in water without decomposition. (Berzelius.)

Oxalate of Bismuth. — Aqueous oxalic acid blackens bismuth, without dissolving it. It combines readily with the hydrated oxide, forming a white powder. From nitrate of bismuth, it throws down, in the course of an hour, transparent many-sided grains, which do not become opaque by immersion in water, and like the white powder, contain 30 per cent of bismuth. (Bergman.) The salt ignited in a close vessel gives off water and carbonic acid, and leaves metallic bismuth. (Boussingault, *Ann. Chim. Phys.* 54, 266.) It contains 62·03 per cent of BiO^3, 9·12 C, 10·1 H and 27·84 O. (Schwarzenberg, *Ann. Pharm.* 64, 12, 6.) [Probably therefore $C^{12}Bi^2O^{24}+6Aq$.]

When the finely pulverized salt is boiled for some time with water, which abstracts the oxalic acid, there remains a white crystalline powder which decomposes between 200° and 240°, with evolution of carbonic acid, is insoluble in cold dilute nitric acid, slightly soluble in strong nitric acid, but dissolves with tolerable facility in hydrochloric acid. (Heintz, *Pogg.* 63, 90.)

			Heintz.
2 BiO^3	474	73·49	72·73
2 C^4O^6	144	22·32	23·10
3 HO	27	4·19	4·15
$2BiO^3,2C^4O^6+3Aq$	645	100·00	99·98

Oxalate of Zinc.—Produced in the form of a white powder: 1. By treating zinc with oxalic acid, the action being attended with rapid

evolution of gas; — 2. By precipitating sulphate, chloride, or nitrate of zinc with oxalic acid, which throws down the zinc completely (Bergman.) — 3. By precipitating zinc-salts with normal oxalate of potash (Schindler, *Mag. Pharm.* 36, 62.) — White, non-crystalline powder (Schindler.) — Gives off all its water above 100°, and afterwards at a stronger heat yields carbonic oxide and carbonic acid, leaving an oxide of zinc possessing peculiar properties. (Dulong.) At a red heat, it gives off equal volumes of carbonic acid and carbonic oxide gases, and leaves yellowish-white oxide of zinc, which does not increase in weight when ignited in the air, and is therefore not a suboxide. (Regnault, *Ann. Chim. Phys.* 62, 354; Pelouze, *Ann. Chim. Phys.* 79, 112.) The residual oxide exhibits no peculiarity, excepting that it sometimes retains a little carbonic acid. (Marchand, *Pogg.* 36, 144.) — Oxalate of zinc is scarcely soluble in water, except in presence of excess of acid. (Bergman.) It dissolves in aqueous hydrochloric acid and in ammonia. (Thompson.) Also in carbonate of ammonia; but the sulphate, hydrochlorate, nitrate and succinate of ammonia dissolve it but imperfectly, even with the aid of heat. (Wittstein, *Repert.* 17, 33.) According to Brett, it dissolves completely in hot sal-ammoniac.

	Air-dried.			Schindler.		Marchand.
2 ZnO	80	....	42·55	42·59	.....	42·93
C^4O^6	72	....	38·30	38·32	.....	37·53
4 HO	36	....	19·15	19·09	.....	19·54
$C^4Zn^2O^8 + 4Aq$	188	....	100·00	100·00	.....	100·00

Zinco-ammonic Oxalate. — *a.* Deposited in needles when oxalic acid is added to an aqueous solution of chloride of zinc supersaturated with ammonia. (Wackenroder, *Ann. Pharm.* 10, 63)

b. When an aqueous solution of acid oxalate of ammonia is digested with carbonate of zinc till it is completely saturated, oxalate of zinc separates out; and the filtrate when evaporated leaves milk-white nodules, which slowly effloresce and give off water, are nearly insoluble in cold water, but are decomposed by hot water, with separation of carbonate of zinc. (Kayser, *Pogg.* 60, 140.)

	b. Crystallized.			Kayser.
4 NH^3	68	....	14·98	16·86
2 ZnO	80	....	17·62	17·58
3 C^4O^6	216	....	47·58	46·24
10 HO	90	....	19·82	
$2[C^4(2NH^4)O^8] + C^4Zn^2O^8 + 6Aq$	454	....	100·00	

Zinc-potassic Oxalate. — A concentrated solution of normal oxalate of potash boiled for some time with oxalate of zinc, and then filtered, yields on cooling, small transparent tables, which effloresce, are nearly insoluble in cold water, and are decomposed by boiling water, with separation of oxalate of zinc. (Kayser.)

				Kayser.
KO	47·2	....	24·18	24·88
ZnO	40·0	....	20·49	18·66
C^4O^6	72·0	....	36·88	
4 HO	36·0	....	18·45	20·66
$C^4ZnKO^8 + 4Aq$	195·2	....	100·00	

Oxalate of Cadmium. — Formed by precipitating a cadmium-salt with alkaline oxalates (Stromeyer), or with free oxalic acid. (Marchand, *Pogg.*

38, 146.) White crystalline powder. (Marchand.) — Does not lose weight in vacuo or when heated to 100°, but when heated in a closed vessel to the melting point of lead, it gives off water, carbonic acid, and carburetted hydrogen gas, and leaves green suboxide of cadmium (V, 53.) If the temperature be suddenly raised above this point, charcoal separates out, and at a red heat exerts a reducing action, so that a mixture of metal and oxide remains behind. (Marchand.) — The salt does not dissolve in water (Stromeyer), even in presence of free oxalic acid (Children); but is easily soluble in a cold aqueous solution of sal-ammoniac (Brett), also in ammonia, and in sulphate, nitrate and succinate of ammonia. (Wittstein.)

			Marchand.
2 CdO	128	54·24	53·81
C^4O^6	72	30·51	30·19
4 HO	36	15·25	16·00
$C^4Cd^2O^8 + 4Aq$	236	100·00	100·00

Stannous Oxalate. — *a. Normal.* Tin immersed in a warm aqueous solution of oxalic acid, blackens at first, and gives off gas, and afterwards becomes covered with a white powder, while a large quantity of tin dissolves in the liquid. (Bergman.) According to Hausmann and Löwenthal, the quantity of tin dissolved is scarcely perceptible. — The precipitate which oxalic acid forms with stannous acetate yields by dry distillation, water, carbonic oxide, carbonic acid, and empyreumatic oil, and leaves light brown stannous oxide. (Boussingault, *Ann Chim. Phys.* 54, 266.) It dissolves in hot hydrochlorate and nitrate of ammonia. (Brett.) Forms shining needles which are insoluble in cold water, and are partly decomposed by boiling water. Forms double salts with the oxalates of ammonia, potash, and soda. (Bouquet, *Ann. Pharm.* 64, 278.)

¶ An aqueous solution of protochloride of tin forms with oxalic acid a white, crystalline, pulverulent precipitate of stannous oxalate containing water, only a small quantity of tin remaining in the liquid. — The salt is permanent in the air, and does not part with all its water at 100°, or even at considerably higher temperatures, 2 or 3 per cent of water obstinately adhering to it, even when it is heated to between 160° and 180° in a current of air. It is very little soluble in water, either hot or cold, insoluble in oxalic acid, sparingly soluble in cold dilute acids, but dissolves readily in hot hydrochloric or nitric acid, in the latter case with evolution of red vapours. The nitric acid solution, when heated for some time, deposits a large quantity of stannic oxide. — Stannous oxalate dissolves in hot solutions of ammoniacal salts, and partly separates out again in small crystals on cooling. It forms double salts with the oxalates of ammonia, potash and soda. (Hausmann and Löwenthal, *Ann. Pharm.* 89, 104.)

		Hausmann & Löwenthal.		
		a.		*β.*
2 SnO	136	65·37	63·56	63·61
C^4O^6	72	34·63	33·64	33·43
HO			2·80	2·91
$2SnO,C^4O^6$ or $C^4Sn^2O^8$	208	100·00	100·00	99·95

a was dried at 100°, *β* at 160°. The mean of these analyses gives for the anhydrous salt, SnO = 65·44; oxalic acid = 34·51. ¶

b. Acid Salt. — Aqueous oxalic acid, after being digested with tin (*vid. sup.*), tastes rough, still reddens litmus, and yields prismatic crystals,

or when the solution is evaporated to dryness, a horny mass, whose aqueous solution forms a copious precipitate with the alkalis. (Bergman.)

Stannic Oxalate. — Stannic oxide dissolves readily in oxalic acid (Bergman.) — ¶ Recently precipitated stannic oxide (obtained by precipitating the chloride with sulphate of soda) dissolves readily in a warm solution of oxalic acid. A solution nearly saturated with stannic oxide — which, as well as the perfectly saturated solution, turns blue on exposure to sunshine even if the air be excluded, but becomes colourless again in the dark—yields on evaporation, shining white laminæ containing variable quantities of stannic oxide, and becoming, by repeated crystallization, continually poorer in that substance, till at length pure oxalic acid crystallizes out in flattened prisms.—The solution saturated with stannic oxide is somewhat milky, and yields, when evaporated, not crystals, but a colourless jelly which dries up to gummy fragments. The dried salt yields by trituration a white powder soluble in water; its composition is not constant, the amount of stannic oxide varying between 72 and 80 per cent. When treated with a small quantity of cold water, it becomes continually more basic.

The solution of stannic oxide in oxalic acid yields with the sulphates, hydrochlorates, nitrates, &c., of the alkalis, a white precipitate of hydrated stannic oxalate, soluble in water. Oxalate of ammonia produces no precipitate. Sulphuric, nitric, and hydrochloric acid at ordinary temperatures produced the same precipitate, soluble in water and in excess of hydrochloric or sulphuric acid. — Ammonia forms the same precipitate, soluble in water and in excess of ammonia. From the ammoniacal solution the precipitate separates again after a while, but is then no longer soluble in ammonia, though still soluble in water, in which however it likewise becomes insoluble, after remaining for some time in contact with the ammoniacal liquid. The fixed alkalis and alkaline carbonates also form white precipitates, soluble in water immediately after precipitation, but becoming insoluble after remaining for some time in the liquid or being heated with it. All these soluble precipitates dry up at 100°, forming gummy fragments, which are afterwards nearly insoluble in water, that liquid merely extracting a little oxalic acid from them, and a trace of stannic oxide. At a red heat, they leave a small quantity of charcoal, and when that is burnt away, a residue of light yellow stannic oxide. They all appear to have the same composition, viz.:

			Hausmann & Löwenthal.	
			a.	*b.*
$12\ SnO^2$	900	83·33	83·64	83·28
C^4O^6	72	6·67	6·64	6·78
12 HO	108	10·00	9·72	9·94
$12SnO^2,C^4O^6+12Aq$	1080	100·00	100·00	100·00

a was precipitated by chloride of ammonium; *b* by cold nitric acid. (Hausmann & Löwenthal.)

Ammonio-stannous Oxalate. — Obtained by dissolving stannous oxalate in a boiling concentrated solution of oxalate of ammonia, and mixing the solution when cold with alcohol. It then, after some time, deposits the double salt in stellate groups of needles which effloresce in the air, are insoluble in alcohol, and have a very sweet taste. The concentrated solution, when left to itself for some time, deposits stannous oxalate. (Hausmann & Löwenthal.)

				Hausmann & Löwenthal.
SnO	68	38·86		38·00
NH^4O	26	14·86		15·60
C^4O^6	72	41·14		40·52
HO	9	5·14		5·88
$C^4Sn(NH^4)O^8 + Aq$	175	100·00		100·00

This salt is isomorphous with the potassium-salt (*inf.*); it fuses and detonates when heated. (Bouquet.)

Potassio-stannous Oxalate. — 1. Obtained by dissolving recently precipitated stannous oxalate in a hot concentrated solution of neutral oxalate of potash. Purified by recrystallization. (Hausmann & Löwenthal.) — 2. By treating acid oxalate of potash with a large excess of stannous oxide. — Transparent, colourless, prismatic crystals which dissolve readily in hot water, less readily in cold water, and are insoluble in alcohol. (Hausmann & Löw.) — Bouquet's salt forms large colourless crystals, which dissolve readily in cold water, forming a solution which becomes milky after a while, and decomposes quickly when boiled, yielding first a white gelatinous, and afterwards a black precipitate. (Bouquet.) — The salt has a strong sweet taste, but leaves a bitter after-taste. It reddens litmus, and is not decomposed when heated to 100° in contact with the air. (Hausmann & Löwenthal.)

				Hausmann & Löwenthal.
SnO	68·0	34·66		34·68
KO	47·2	24·05		24·35
C^4O^6	72·0	36·70		36·30
HO	9·0	4·59		4·67
$C^4SnKO^8 + Aq$	196·2	100·00		100·00

Sodio-stannic Oxalate. — Prepared like the potassium-salt, which it resembles in its properties. (Hausmann and Löwenthal.) Anhydrous and crystallizable. (Bouquet.) ¶

Oxalate of Lead. — *a. Basic.* — Obtained in the form of a white powder, by precipitating an aqueous solution of trisacetate of lead with normal oxalate of ammonia, or by boiling the normal oxalate of lead with the aqueous solution of the trisacetate (which is thereby converted into the normal acetate), — and in white shining laminæ, soft to the touch, by mixing a boiling solution of oxamide with nitrate or acetate of lead, and then with a small quantity of ammonia. — When exposed to the air, it absorbs carbonic acid, and is resolved into a mixture of carbonate and normal oxalate of lead. Acetic acid dissolves out the excess of oxide of lead; so does a boiling solution of nitrate of lead, being itself thereby converted into a basic nitrate. (Pelouze, *Ann. Chim. Phys.* 79, 104; also *Ann. Pharm.* 42, 206; also *J. pr. Chem.* 25, 487.)

				Pelouze.
6 PbO	672	90·32		90·5
C^4O^6	72	9·68		9·5
$4PbO + C^4Pb^2O^8$	744	100·00		100·0

b. Normal. — Precipitated in the form of a white powder by adding oxalic acid to any solution of a lead-salt. (Bergman.) May also be obtained in needles. (Berzelius, *Lehrb.*) — When cautiously heated in a retort, it gives off carbonic acid mixed with a smaller quantity of carbonic

oxide, and leaves suboxide of lead. (Dulong, Boussingault, Pelouze V, 107.) The decomposition takes place at 300°, and yields continually 3 vol. carbonic acid gas to 1 vol. carbonic oxide; towards the end only, if the heat be raised somewhat above 300° to complete the decomposition, the proportion of carbonic acid becomes somewhat greater (Pelouze):

$$C^4Pb^2O^8 = Pb^2O + 3CO^2 + CO.$$

A mixture of the dry salt with pieces of potassium detonates violently below the temperature at which the lead-salt alone is decomposed; the tube, which is broken by the explosion, is afterwards found to contain lead and potash, but no charcoal. (Serullas, *J. Pharm.* 12, 575.) — The salt is insoluble in water, but dissolves sparingly in aqueous oxalic acid (Bergman); it is insoluble in acetic acid. (Vauquelin.) It dissolves in warm aqueous sal-ammoniac (Brett); also in boiling nitrate and succinate of ammonia, but not in caustic ammonia or carbonate of ammonia. (Wittstein, *Repert*, 63, 330.) Soluble in nitric acid.

	Dried at 140°.			Berzelius. (*Ann. Chim.* 94, 180.)		(*Pogg.* 47, 199.)
2 PbO	224	....	75·676	75·46	.....	75·479
CO	72	....	24·324	24·54	.....	24·521
$C^4Pb^2O^8$	296	....	100·000	100·00	.....	100·000

Oxalo-nitrate of Lead. — *a. Basic.* — $4PbO,C^4Pb^2O^8 + 6(PbO,NO^5) + 6Aq$. — When oxamide is boiled with a strong solution of nitrate of lead mixed with ammonia, this salt is precipitated during the ebullition in white, shining, crystalline grains, which must be washed with cold water and dried in vacuo. If the boiling be too long continued, and the liquid still contains neutral nitrate of lead (which thereby becomes bibasic,) the salt is converted into the following salt *b*. The salt *a* is likewise formed when basic oxalate of lead is boiled with a solution of nitrate of lead in a double quantity of water, the ebullition being stopped before the salt *a* is converted into *b*. (Pelouze, *Ann. Chim. Phys.* 79, 104.)

b. Normal. — $C^4Pb^2O^8 + 2(PbO,NO^5) + 4Aq$. — Discovered by Johnston, (*Phil. Mag. J.* 13, 25; *N. Br. Arch.* 15, 166,) and by Dujardin (*Institut.* 1838, January; also *J. pr. Chem.* 15, 308.) — 1. Formed by adding a solution of normal acetate of lead to a mixture of dilute oxalic acid with a large quantity of nitric acid, — or dilute oxalic acid to a mixture of a dilute solution of normal acetate of lead and a large quantity of nitric acid; or by mixing lead-vinegar with a large quantity of nitric acid, and slowly adding dilute oxalic acid. The double salt is then precipitated after a while in shining laminæ, the precipitation becoming slower as the quantity of oxalic acid in the liquid diminishes. (Johnston.) — 2. The salt likewise separates from a solution of oxalate of lead in warm dilute nitric acid. (Dujardin.) — 3. It is also formed by boiling normal oxalate of lead with a strong solution of the nitrate. (Pelouze.) The crystals must not be washed with water. (Johnston.) — White, nacreous, six-sided laminæ, whose faces are longitudinally striated, or long needles (Johnston); oblique rhombic prisms (Miller); rhombic tables (Dujardin); hexagonal tables (Pelouze).

	Crystallized.			Johnston.
4 PbO	448	....	67·47	..... 67·28
$2 NO^5$	108	....	16·27	
C^4O^3	72	....	10·84	
4 HO	36	....	5·42	..... 5·28
$C^4Pb^2O^8 + 2(PbO,NO^5) + 4Aq$	664	....	100·00	

The salt loses nothing at 100°, but gives off 5·28 per cent of water towards 260°; at a temperature somewhat below 300°, it evolves nitrous fumes and leaves carbonate of lead, which at a higher temperature is converted into the oxide. (Johnston, Dujardin.) It is decomposed by water, the decomposition taking place with peculiar facility if the salt has not been previously dried at 100°. Boiling water dissolves out nearly all the nitrate of lead, leaving 52·35 per cent of a mixture of oxalate of lead and a small quantity of undecomposed double salt. (Johnston.) Cold water decomposes the salt slowly, boiling water quickly. (Pelouze.) The salt dissolves in warm nitric acid, and separates again on cooling. (Dujardin.)

Potassio-plumbic Oxalate. — Acid oxalate of potash digested with hydrated oxide of lead, dissolves a small portion of it, and yields small needles which are permanent in the air, but are decomposed by alkalis. (Wenzel.)

Plumbo-chromic Oxalate.—$3(PbO,C^2O^3) + Cr^2O^{33}3C^2O^3 + 15Aq[= C^{12}Pb^3 Cr^2,O^{24} + 15$ Aq.]—A solution of blue potassio-chromic oxalate forms with normal acetate of lead, a bluish grey precipitate, which does not lose weight at 100°; while still moist, it dissolves in boiling chromic oxalate, but separates again unchanged on cooling. (Berlin.)

Ferrous Oxalate. — *a. Normal.* Found in brown coal strata in the form of *Humboldtite* or *Iron-resin;* yellow, of sp. gr. 2·13; rarely in capillary crystals; generally in crude masses of fibrous, granular, or compact texture, somewhat harder than gypsum. (Breithaupt, *Gilb.* 70, 426) Mariano de Rivero and Vauquelin, *Ann. Chim. Phys.* 18, 207; abstr. *Schw.* 33, 426.)

Preparation. Iron dissolves in aqueous oxalic acid, with evolution of hydrogen, forming at first an acid salt; but as the acid becomes further saturated with ferrous oxide, the normal salt is precipitated. (Berzelius, *Lehrb.*) — 2. The salt is also obtained by precipitating green vitriol with oxalic acid. (A. Vogel, *J. pr. Chem.* 6, 339.) The iron is almost wholly precipitated; if the filtrate be afterwards evaporated, the last portions of ferrous oxalate settle down, and the liquid filtered therefrom contains nothing but sulphuric acid and a trace of iron. (A. Vogel.) — 3. By precipitating green vitriol with normal oxalate of potash. (Rammelsberg, *Pogg.* 46, 283; 53, 633; 68, 276). — 4. When a solution of ferric oxalate in aqueous oxalic acid is exposed to the sun, carbonic acid is evolved, and ferrous oxalate precipitated. (Döbereiner, *Schw.* 62, 90.) Döbereiner calls this precipitate, *Lichthumboldite.*

Prepared by (2) it is a yellow powder (A. Vogel); by (4): small lemon-yellow shining crystals. (Döbereiner.)

	Native.			Rammelsb.	Vauquelin.
2 FeO	72	....	42·11	..... 41·13	..... 53·86
C^4O^6	72	....	42·11	..... 42·40	
3 HO	27	....	15·78	..... 16·47	
$C^4Fe^2O^8 + 3Aq$	171	....	100·00	..... 100·00	

	Artificial.			Rammelsb. (3).
2 FeO	72	....	40	..... 38·98
C^4O^6	72	....	40	
4 HO	36	....	20	
$C^4Fe^2O^8 + 4Aq$	180	....	100	

Döbereiner, at an earlier date than Rammelsberg, found also 4Aq. in his Lichthumboldite.

The salt, when ignited in a retort after thorough drying, is for the most part resolved into water, carbonic acid, carbonic oxide, and a mixture of ferroso-ferric oxide with iron containing a small quantity of charcoal. According to Magnus (*Pogg.* 3, 88), the residue consists of metallic iron. The salt obtained by (4) gives off at first 21·6 per cent of water, then a mixture of 2 vol. carbonic oxide and 3 vol. carbonic acid gas, and leaves 39 per cent of a greyish black pyrophoric powder, consisting of ferrous oxide and carbide of iron, which when strongly ignited in a retort, gives off carbonic oxide, and is converted into a mixture of iron and ferrous oxide. (Döbereiner, *Schw.* 62, 96.) — Carbonic acid and carbonic oxide are evolved, and the residue consists of ferroso-ferric oxide, which dissolves in hydrochloric acid without evolution of hydrogen, in aqua-regia without leaving any carbonaceous residue, and does not diminish in weight by ignition in the air. (Böttger, *Beiträge*, 2, 43.) — The salt (3) leaves 41·83 per cent of residue, which, when ignited in the air, yields a quantity of ferric oxide amounting to 44·31 p.c. of the salt, and a quantity of carbonic acid corresponding to 0·33 per cent of carbon. But 100 pts. of the salt contain 31·11 iron; and deducting this quantity of iron and the 0·33 carbon from the 41·83 p.c. of residue, there remains 10·39 for the quantity of oxygen therein. — The residue, therefore, neglecting the 0·33 p.c. carbon, is Berthier's ferroso-ferric oxide Fe^4O^7 (V, 190): for, 10·39 (oxygen) : 31·11 (iron) = 7 . 8 : 167 (and 6 . 28=168.) — Lastly, since 100 pts. of the salt contain 13·33 pts. carbon and 35·56 oxygen (besides that of the water), and 0·33 pt. of the carbon and 10·39 of the oxygen remain in the residue, it follows that 13 pts. of carbon and 25·17 of oxygen have been evolved, doubtless as a mixture of about 5 vol. carbonic oxide and 4 vol. carbonic acid [or more exactly 10 : 9]. Rammelsberg.

An aqueous solution of carbonate of potash or soda abstracts the oxalic acid from the native salt; ammonia also produces this effect with peculiar facility (Rivero & Vauquelin); caustic potash and carbonate of potash decompose the artificial salt in a similar manner. (A. Vogel.) The salt boiled with aqueous phosphate of soda produces oxalate of soda and ferrous phosphate. — The native salt is insoluble in water (Rivero & Vauquelin); the artificial salt is scarcely soluble in cold water, and dissolves very sparingly in boiling water. (A. Vogel.) It is insoluble in oil of vitriol, but dissolves in warm dilute sulphuric acid, which again deposits the light yellow powder when evaporated. It dissolves in cold concentrated hydrochloric acid, is scarcely soluble in cold aqueous oxalic acid, and dissolves but sparingly in the boiling acid. (A. Vogel.)

b. Acid Salt? — Iron immersed for some time in aqueous oxalic acid, eliminates hydrogen, and forms a sweet, astringent liquid which deposits yellow-green acid prisms, efflorescing when heated, and easily soluble in water. (Bergman.) — This does not agree with the above statement by Vogel, respecting the slight solubility of the normal salt in oxalic acid. The discrepancy may perhaps be reconciled by Berthier's observation, that an aqueous solution of acid ferric oxalate dissolves a large quantity of ferrous-oxalate; so that Bergman's crystals perhaps consist of ferroso-ferric oxalate, — a supposition agreeing, indeed, with Barreswil's suggestion that the green oxalate of iron is a ferroso-ferric salt.

Ferric Oxalate. a. Normal. — Obtained by treating hydrated ferric oxide with oxalic acid not in excess (Bergman), or by treating a ferric salt with an alkaline oxalate not in excess, which slowly forms a preci-

pitate. (Bucholz, *N. Gehl.* 2, 678.)—Lemon-yellow powder, nearly insoluble in water, and separating in the form of an ochre when boiled with water.

b. Acid. — The salt *a* dissolves in aqueous oxalic acid. (Laugier.) The acid solution remains unaltered in the dark, even at 100°; but in solution, or more slowly in ordinary daylight, it turns greenish yellow, continually gives off carbonic acid, and deposits crystals of ferrous oxalate, till all the iron is converted into that salt, and the liquid is decolorized (Döbereiner, *Schw.* 62, 90):

$$C^{12}Fe^4O^{24} = 2(C^4Fe^2O^8) + 4CO^2.$$

The acid solution is capable of dissolving a large quantity of manganous or ferrous oxalate. (Berthier, *Ann. Chim. Phys.* 50, 89.)

Ammonio-ferric Oxalate. — The green solution of hydrated ferric oxide in warm aqueous acid oxalate of ammonia yields, on cooling, small slightly rhombic octohedrons. The salt, when exposed to light, turns yellowish by formation of ferrous oxalate; this change is especially quick in the powder, the greenish white colour of which changes almost instantly to ochre-yellow in sunshine; the aqueous solution also, when exposed to sunshine, gives off carbonic acid, becomes decolorized, and deposits ferrous oxalate in the form of a yellow powder. The salt dissolves in 1·1 pt. of water at 20°, and in 0·79 pt. of boiling water.

	Crystallized.			Bussy.	
$3\,NH^3$	51	....	13·64		
Fe^2O^3	80	....	21·38	.....	21·00
$3\,C^4O^6$	216	....	57·76	.....	57·85
$3\,HO$	27	....	7·22		
$C^{12}(3NH^4,Fe^2)O^{24}$	374	....	100·00		

¶ Calculation according to Rammelsberg.				Rammelsberg.		
$3\,NH^4O$	78	....	18·22			
Fe^2O^3	80	....	18·71	.....	17·48	18·10
$3\,C^4O^6$	216	....	50·46			
$6\,HO$	54	....	12·61			
$C^{12}(3NH^4,Fe^2)O^{24}+6Aq$	428	....	100·00			

Bussy's analysis and the corresponding calculation cannot refer to the crystallized salt, since they do not include the water of crystallization. (Rammelsberg.) ¶

Potassio-ferric Oxalate. — 1. Obtained by dissolving hydrated ferric oxide to saturation in solution of salt of sorrel, then filtering and cooling. (Wenzel, *Verwandtschaft*, 318; Bussy, Graham.) It is the formation of this soluble salt which renders salt of sorrel useful in removing rust-spots. — 2. A mixture of aqueous sesquichloride of iron and normal oxalate of potash, deposits at first the yellow pulverulent ferric oxalate, afterwards the double salt. (Bucholz, *N. Gehl.* 9, 679.)—Dark green rhomboïdal crystals. (Wenzel.) Small, apple-green, flat, four-sided prisms, with dihedral summits, and having a sweet, slightly ferruginous taste. (Bucholz.) Large, emerald-green crystals, having an astringent, somewhat sweetish taste (Bussy.) Apple-green laminæ. (Graham.) The crystals are modified rhombic prisms belonging to the oblique prismatic system (Rammelsberg, *Pogg.* 93, 44.)—They effloresce in the air, and, whether in the free state, or in the state of aqueous solution, are decomposed by light in the same manner as the ammonia double salt. (Bussy.) They effloresce only in very dry air, becoming brown and opaque. (Graham.) At 100°, they give off 11·12 per cent of water

(Bussy); 10·56 p.c. (Graham); and are partially decomposed at 160°. (Graham.) The salt begins to decompose at 300°, and is converted, with evolution of carbonic acid, into a yellow powder, which appears to be a mixture of oxalate of potash and ferrous oxalate, inasmuch as it dissolves in water, at first, but soon afterwards deposits ferrous oxalate, while potassio-ferric oxalate remains in solution. (Bussy.) — The crystals dissolve in 14·3 pts. of cold and 4 pts. of boiling water, forming a green solution (pale yellow-green, according to Bucholz) which reddens litmus (Bussy):

	Crystallized.			Bussy.	Graham.	Rammelsberg.
3 KO	141·6	28·80		28·62	29·07	27·97 .... 26·94
Fe^2O^3	80·0	16·27		16·00	16·13	16·06 .... 16·19
$3\ C^4O^6$	216·0	43·94			43·74	
6 HO	54·0	10·99		11·12	10·56	
$C^{12}K^3Fe^2O^{24}$	491·6	100·00			99·50	

Mitcherlich (*Pogg.* 43, 126), mentions a similar double salt, in which however the oxygen of the ferric oxide amounts to three times that of the potash, and which, when ignited, leaves a compound of ferric oxide and potash free from carbonic acid. — The solution of ferric oxide in hyperacid oxalate of potash dries up by evaporation to a brown gum. (Croft, *Phil Mag. J.* 21, 200.)

Sodio-ferric Oxalate. — The solution of hydrated ferric oxide in aqueous acid oxalate of soda, yields large, emerald-green crystals, which give of 12·2 p.c. water at 300°. (Bussy.) The crystals belong to the oblique prismatic system, but are not isomorphous with the potash-salt; they are rhombic or rhomboïdal tables having their edges truncated and bevelled. (Rammelsberg.) They give off 4 At. water at 100°, retaining 6 At. (Graham.) The dry salt decomposes at 300°, just like the potassio-ferric salt. (Bussy.) It dissolves in 2 pts. of water at 20°, and in 0·6 pt. of boiling water. (Bussy.)

Calculation, according to Bussy.			Bussy.
3 NaO	93·6	21·10	20·97
Fe^2O^3	80·0	18·04	17·33
$3\ C^4O^6$	216·0	48·69	
6 HO	54·0	12·17	12·20
$C^{12}Na^3Fe^2O^{24} + 6Aq$.	443·6	100·00	

Calculation, according to Graham.			Graham.
3 NaO	93·6	19·52	19·66
Fe^2O^3	80·0	16·68	16·56
$3\ C^4O^6$	216·0	45·03	45·51
10 HO	90·0	18·77	18·27
$C^{12}Na^3Fe^2O^{24} + 10Aq$	479·6	100·00	100·00

Calculation, according to Rammelsberg.			Rammelsberg.
3 NaO	93·6	19·87	19·19
Fe^2O^3	80·0	17·02	17·12
$3\ C^4O^6$	216·0	45·90	46·44
9 HO	81·0	17·21	
$C^{12}Na^3Fe^2O^{24} + 9Aq$	470·6	100·00	

Baryto-ferric Oxalate. — $C^{12}Ba^3Fe^2O^{24} + 7Aq.$ and $+ 21Aq.$ — Prepared by precipitating ammonio-ferric oxalate with chloride of barium,

and purifying the precipitate by crystallization from hot water. Greenish yellow needles having a silky lustre. Both in the dry state and in their aqueous solution, they are decomposed by sunshine, with evolution of carbonic acid. Ammonia, potash and soda abstract the acid from the ferric oxide, and separate that oxide together with oxalate of baryta. The crystals are scarcely soluble in cold water, but dissolve in 30 parts of boiling water. (Rees Reece.)

Strontio-ferric Oxalate. — $C^{12}Sr^3Fe^2O^{24} + 18Aq$. — Similar to the baryta-salt. (Reece.)

Calcio-ferric Oxalate. — Similar in composition; but its amount of water cannot be ascertained, because it does not crystallize. In other respects it exhibits similar relations to the baryta-salt. In consequence of the formation of this somewhat soluble salt, lime is not precipitated by oxalic acid from its acid solutions which likewise contain ferric oxide, unless indeed the solution be highly concentrated, and even then the precipitation is imperfect; to obtain complete precipitation, it is necessary to adopt the process recommended in the case of calcio-chromic oxalate (p. 142). (Reece.)

Cobaltous Oxalate. a Basic. — Obtained by the action of potash on the normal salt diffused in water, which has been thoroughly freed from air by boiling and then cooled in a close vessel. The product is a blue salt, which remains blue even when treated with a very large excess of potash, not being thereby deprived of the whole of its oxalic acid until it is heated; it is then rapidly converted into the red hydrated protoxide. By washing the precipitate with thoroughly boiled water out of contact of air, pressing it between paper, and drying in vacuo, the salt is obtained in the form of a bluish green powder which, when ignited in close vessels, gives off water and carbonic acid, and leaves a mixture of metal and protoxide. (Winckelblech, *Ann. Pharm.* 13, 158.)

				Winckelblech.
6 CoO	225	....	67·57	..... 67·55
C^4O^6	72	....	21·62	..... 22·08
4 HO	36	....	10·81	..... 10·37
$4CoO,C^4Co^2O^8 + 4Aq$	333	....	100·00	..... 100·00

b. Normal. — Formed by the action of cold aqueous oxalic acid on metallic cobalt (Bergman); precipitated on mixing other dissolved cobalt-salts with oxalic acid or oxalate of potash. It is best obtained by digesting carbonate of cobalt with excess of aqueous oxalic acid, which dissolves but little of the oxalate of cobalt, but removes any ferric oxide that may be present. (Langier.) Rose-coloured powder which does not redden litmus. — The air-dried salt is $CoO,C^2O^3 + 2Aq$. ($= C^4Co^2O^8 + 4Aq$.), and may be completely freed from water by carefully heating; but when further heated in the air, it takes fire and leaves cobaltic [cobaltoso-cobaltic] oxalate. The air-dried salt, when heated to redness out of contact of air, is resolved into 19·57 per cent of water, 47·57 carbonic acid, and 32·86 metallic cobalt. (Döbereiner, *Schw.* 28, 161.) — The salt is nearly insoluble in water and in aqueous oxalic acid; according to Winckelblech, it requires 40,000 pts. of boiling aqueous oxalic acid to dissolve it. In aqueous ammonia it dissolves with tolerable facility, and still more readily in carbonate of ammonia. It likewise dissolves to a slight amount in hot aqueous sulphate, hydrochlorate, nitrate or succinate

of ammonia, imparting a light red colour to the liquid, and separating out again on cooling. (Wittstein, *Repert.* 57, 35).

			Döbereiner.	Winckelblech.
2 CoO	75	40·99	41·77	41·22
C^4O^6	72	39·34		39·59
4 HO	36	19·67	19·57	19·62
$C^4Co^2O^8 + 4Aq$	183	100·00		100·43

Cobaltoso-cobaltic Oxalate. — Aqueous oxalic acid placed in contact with hydrated sesquioxide of cobalt, yields a dark green solution of the cobaltoso-cobaltic salt, carbonic acid being at the same time evolved, and a small quantity of cobaltous oxalate separated out; the green solution evaporated under a bell-jar over oil of vitriol, yields dark green silky needles, which easily redissolve in water with the colour of aqueous manganate of potash. The solution slowly decomposes, even below 50°, into carbonic acid and cobaltous oxalate; and if it be exposed to light, the same decomposition takes place in a few months at ordinary temperatures, the cobaltous salt then separating in small crystals. Sulphuretted hydrogen exerts but a slow decomposing action on the green solution. Potash added to the solution forms a brown precipitate; carbonate of potash, a green precipitate which turns brown in the air, probably giving off carbonic acid at the same time. Ammonia forms a brown precipitate, but only with strong solutions. The carbonates of baryta and lime do not decompose the salt, but merely remove the excess of oxalic acid. Hydrochlorate or nitrate of lime forms no precipitate. Cyanide of potassium forms a white precipitate, probably consisting of a corresponding cyanide. Ferrocyanide of potassium gradually produces, especially in the acid solution, a blue precipitate resembling Prussian blue.

	Anhydrous.	
Co^3O^4	120·5	45·56
2 C^4O^6	144·0	54·44
$C^8Co^3O^{16}$	264·5	100·00

$= CoO,C^2O^3 + Co^2O^3,3C^2O^3$, seeing that, on boiling the solution, cobaltous oxalate is formed, and ⅓ of the carbon contained in the oxalic acid escapes in the form of carbonic acid. (Winckelblech).

Cobaltous Oxalate with Ammonia. — Cobaltous oxalate dissolves with red colour in aqueous ammonia, sparingly in a dilute, more copiously in a strong solution, more quickly when heated; and yields when evaporated in an open vessel, red laminæ, needles and nodules, which dissolve readily in cold, more readily in hot water, and leave cobaltic [cobaltoso-cobaltic] oxide when ignited in the air. (Laugier). — Cobaltous oxalate shaken up with warm aqueous ammonia in a stoppered bottle, dissolves completely in 30 times its quantity of that liquid. If the air has access to the liquid, and the process is not very quickly performed, part of the cobalt separates in a more highly oxidized state as a dingy violet powder, which does not dissolve even in a large quantity of boiling aqueous ammonia, but merely gives up oxalic acid to it, becomes continually browner, and after washing, gives off chlorine with hydrochloric acid and ammonia with potash. (Winckelblech). — The ammoniacal solution forms a blue precipitate with potash; when evaporated in the air, it deposits bright red crystalline crusts, which dissolve in water, though with separation of a large quantity of brown cobaltic oxide, forming a liquid which yields with potash a pre-

cipitate of an impure blue colour, and therefore not containing pure cobaltous oxide (Winckelblech. *Ann. Pharm.* 13, 273).

Cobaltous oxalate, before dissolving in ammonia, takes up a portion of that substance, and acquires a deep red colour, but when separated from the liquid by filtration, and then dried, gives off ammonia, recovers its light red colour, and is then found to contain the same quantity of water that it did before being treated with ammonia (Winckelblech).

Ammonio-cobaltous Oxalate. — Cobaltous oxalate dissolves in aqueous normal oxalate of ammonia, slowly in the cold, but quickly when heated, and forms a carmine-coloured solution, which deposits nothing on cooling, but when left to evaporate spontaneously yields small pale-red crystals. These crystals, as well as the mother-liquor, are neutral, effloresce on the surface, and turn white on exposure to the air, and when ignited in a close vessel, melt, turn blue, and yield 4·01 per cent of metallic cobalt in laminæ, having a steel-like lustre. This salt is but sparingly soluble in cold water, but dissolves in all proportions in boiling water. 1 part of the salt imparts to 50 parts of water a deeper red colour than the salt itself possesses. Since the crystals contain 4·98 per cent of cobaltous oxalate and 47·20 of hypothetical anhydrous oxalic acid, their formula is probably $9(NH^3, C^2O^3) + CoO, C^2O^3 + 24Aq$. (Winckelblech).

The solution of this salt becomes decolorized in a few minutes on the addition of ammonia, and deposits nearly all the cobalt as a light brown powder. This *basic double salt* yields by ignition, ammonia and 27·36 per cent of pulverulent metal; heated with potash, it gives off ammonia, with separation of blue protoxide; it is insoluble in water and dissolves but partially in ammonia. Contains 34·71 per cent of protoxide of cobalt, and 32·99 p.c. hypothetical anhydrous oxalic acid; its formula is probably therefore: $3NH^3, 6CoO, 6C^2O^3 + 18Aq$. (Winckelblech). [$= NH^3, 2CoO, 2C^2O^3 + 6Aq. = NH^3, C^4Co^2O^8 + 6Aq$].

Cobaltic Oxalate with Ammonia. — A solution of cobaltous oxalate in strong ammonia, set aside in vessels containing air or oxygen, and protected from carbonic acid, gradually deposits large, shining, many-faced granules of a hyacinth-red colour. They may be purified by dissolving them in a hot aqueous solution of carbonate of ammonia, then filtering and cooling. They give off 1·17 per cent at 100°; when more strongly heated, they decrepitate slightly, and give off ammonia, turning violet and afterwards black; and when heated to redness in a close vessel, give off steel-grey cobalt, having the form of the crystalline fragments, but very much shrunk. — When boiled with potash, they give off ammonia, with separation of the brown hydrated sesquioxide. They are scarcely soluble in water or aqueous ammonia, but dissolve with tolerable facility in hot carbonate of ammonia (Gm.).

	Air-dried crystals.			Gm.
12 NH^3	204	....	31·87	..... 30·36 to 31·83
12 C	72	....	11·25	..... 10·70 ,, 10·84
4 Co	118	....	18·44	..... 18·05 ,, 18·74
24 O	192	....	30·00	
6 Aq	54	....	8·44	
$12NH^3 + C^{12}Co^4O^{24} + 6Aq$	640	....	100·00	

100 pts. of the salt burnt with oxide of copper (with copper filings at the open end of the tube) yield 30·21 to 39·75 pts. of carbonic acid and 58·23 to 59·83 of water; calculation gives 59·06. Hence the salt is not an oxycobaltate of ammonia as the author at first imagined.

Ammonio-cobaltoso-cobaltic Oxalate. — Obtained by mixing the green solution of cobaltoso-cobaltic oxalate with normal oxalate of ammonia, and evaporating in vacuo. Very small green crystals dissolving very easily in water (Winckelblech).

Cobaltous oxalate dissolves pretty freely in aqueous *carbonate of ammonia*. The carmine-coloured solution does not yield any deposit when exposed to the air.

Basic Potassio-cobaltous Oxalate. — When cobaltous oxalate is dissolved in a boiling solution of normal oxalate of potash, this salt separates on cooling in rose-coloured rhombic crystals. It is also formed when a solution of potassio-cobaltosocobaltic oxalate is left to evaporate for a long time over oil of vitriol. The crystals, when ignited, become blue for a while and leave cobalt mixed with carbonate of potash. They are insoluble in water (Winckelblech, *Ann. Pharm.* 13, 166).

Potassio-cobaltosocobaltic Oxalate. — Obtained by mixing the green solution of cobaltosocobaltic oxalate with normal oxalate of potash, and quickly evaporating in vacuo over oil of vitriol. Very small green crystals, dissolving with great facility in water. When kept for a long time in vacuo, they are resolved into carbonic acid gas and the preceding salt (Winckelblech).

Oxalate of Nickel. — The aqueous acid does not attack the metal, but combines with the hydrate and carbonate when heated; it precipitates the protoxide of nickel from all its simple salts so completely, that only a small quantity of nickel-oxalate remains dissolved in the liberated acid; but the double salts are not completely decomposed by it. Normal oxalate of ammonia, potash, or soda does not precipitate nickel-salts (Tupputi). With oxalate of potash a precipitate is formed after a while, its formation failing only when the potash-salt is in excess (Gm.). —Greenish white flocks, tasteless at first, but afterwards exhibiting a slight metallic taste (Tupputi). The dry salt heated in closed vessels yields 19·43 per cent of water, 45·86 carbonic acid, and 32·14 metallic nickel: hence it is $NiO,C^2O^3+2Aq[=C^4Ni^2O^8+4Aq]$. The salt heated in contact with air, first gives off water, then takes fire, and leaves a black residue of oxide (Döbereiner, *Schw.* 26, 384; 28, 160). — It is insoluble in water and very sparingly soluble in aqueous oxalic acid, but dissolves with tolerable facility in the stronger mineral acids (Tupputi, *Ann. Chim.* 78, 162). Dissolves readily in caustic ammonia and carbonate of ammonia, and incompletely in sulphate, hydrochlorate, nitrate, and succinate of ammonia (Wittstein, *Repert.* 57, 36).

Oxalate of Nickel with Ammonia. — 1. The violet-blue solution of nickel-oxalate in aqueous ammonia, gradually loses its colour, and gives off ammonia when exposed to the air, depositing pale bluish green crusts composed of delicate needles united in tufts (Laugier). — 2. The aqueous solution of ammonio-nickel oxalate (*vid. inf.*) mixed with a small quantity of ammonia, deposits the same salt in the form of a very pale green precipitate, which becomes still paler when dry (Winckelblech). The salt when ignited in a closed vessel, leaves nickel containing charcoal; it is insoluble in water, but dissolves in ammonia (Laugier). With potash it evolves ammonia (Winckelblech, *Ann. Pharm.* 13, 278).

				Winckelblech.		
				Prep. 1.		*Prep.* 2.
NH^3	17	....	7·80	7·55	....	7·51
2 NiO	75	....	34·40	32·88	....	32·52
C^4O^6	72	....	33·03	31·71	....	31·91
6 HO	54	....	24·77	27·72	....	27·57
$NH^3 + C^4Ni^2O^8 + 6Aq$	218	....	100·00	99·56	....	99·51

Winckelblech trebles the formula, making it: $3NH^3,2C^2O^3 + 2(3NiO,2C^2O^3) + 18Aq$.

Ammonio-nickel Oxalate. — Aqueous normal oxalate of ammonia dissolves oxalate of nickel, and the solution yields green prisms by evaporation (Tupputi). The salt which separates from the pale green solution has a still paler green colour, is acted upon by heat and by water like the corresponding cobalt-salt, and appears to have the same composition, inasmuch as it contains 4·76 per cent of nickel-oxide. The aqueous solution mixed with a small quantity of ammonia yields a very pale green precipitate of the preceding compound, which redissolves in excess of the ammonia (Winckelblech).

Potassio-nickel Oxalate. — The solution of nickel-oxalate in boiling normal oxalate of potash, yields green prisms when evaporated (Tupputi); according to Winckelblech, it yields a light-green neutral double salt insoluble in water.

Cuprous Oxalate. — Oxalic acid added to a solution of cuprous chloride in hydrochloric acid, throws down this salt, white at first, but changing after a while to blue green (H. Rose, *Anal. Chem*). Oxalate of potash also precipitates the salt in the form of a white powder, which dissolves readily in ammonia and carbonate of ammonia, and incompletely in sulphate, hydrochlorate, nitrate and succinate of ammonia (Wittstein, *Repert.* 57, 38).

Cupric Oxalate.. — The aqueous acid exposed to the air in contact with the metal, slowly forms cupric oxalate as a pale blue powder. (Bergman.) From an aqueous solution of cupric sulphate, it throws down half the copper in the form of oxalate (Thomson). According to A. Vogel (*J. pr. Chem.* 6, 342,) it throws down the whole; for the liquid decanted from the precipitate and evaporated to a syrup, deposits a small additional quantity of cupric oxalate, and afterwards behaves like oil of vitriol free from copper. — Normal alkaline oxalates added, not in excess, to cupric salts, also form a precipitate of cupric oxalate. According to Hausmann & Löwenthal, it throws down nearly all the copper. — Light greenish blue powder. — The salt, when thoroughly dried and then ignited in the air, leaves 50 per cent of cupric oxide (F. C. Vogel). It may be completely dehydrated by careful heating, and is then entirely resolved at a higher temperature into carbonic acid and metallic copper (Döbereiner). It does not give off all its water at 100°, and consequently when more strongly heated, yields water as well as carbonic acid and metal (Dulong). Decomposition takes place even at a gentle heat, and the residual, perfectly metallic copper, assumes the form of red, shining, malleable laminæ, which are several millimetres thick, although they have been produced from a pulverulent, non-fusing salt (Pelouze, *Ann. Chim. Phys.*, 49, 112).

The salt is neither dissolved nor decomposed by warm nitric acid.

(Dujardin, *J. pr. Chem.* 15, 309.) In oil of vitriol it remains blue. (A. Vogel.) A cold solution of carbonate of potash gives it an azure-blue colour; a boiling solution of that salt turns it black (A Vogel). With potassium it behaves like oxalate of lead (Serullas). — It is insoluble in water, and nearly insoluble in boiling aqueous oxalic acid, but dissolves in warm concentrated hydrochloric acid, forming a yellow solution (A. Vogel). It dissolves, with blue colour, in ammonia and carbonate of ammonia, and with blue-green colour in succinate of ammonia, — likewise, though imperfectly, in sulphate, hydrochlorate, and nitrate of ammonia (Wittstein). It is insoluble in hydrochlorate and nitrate of ammonia (Brett). It dissolves in the aqueous solution of normal oxalate of ammonia, potash and soda (F. C. Vogel).

	Dried at 100°.		Hausmann & Löwenthal.
2 CuO	80	47·06	47·77
C^4O^6	72	42·35	41·74
2 HO	18	10·59	10·49
$C^4Cu^2O^8 + 2Aq$	170	100·00	100·00

Cupric Oxalate with Ammonia. — *a. With* 2 *At. Ammonia.* — When a solution of cupric oxalate in aqueous ammonia is evaporated, this salt separates in short, flat, six-sided prisms of a dark sky-blue colour. Effloresces, giving off 15 per cent of water and ammonia; suffers the same loss of weight at 100°; at higher temperatures it takes fire and explodes (F. C. Vogel).

			F. C. Vogel.
$2 NH^3$	34	16·67	
2 CuO	80	39·22	39·00
C^4O^6	72	35·29	36·00
2 HO	18	8·82	
$2NH^3,C^4Cu^2O^8 + 2Aq$	204	100·00	

b. With 1 *At. Ammonia.* — Cupric oxalate introduced into aqueous ammonia in larger quantity than the ammonia can dissolve, yields, not only the salt *a* in solution, but also the salt *b* in the form of an azure-coloured, sandy powder, which gives off ammonia above 100°, and burns at a stronger heat, with flame and detonation (F. C. Vogel).

	Crystallized.		F. C. Vogel.
NH^3	17	10·06	
2 CuO	80	47·34	45·58
C^4O^6	72	42·60	43·00
$NH^3,C^4Cu^2O^8$	169	100·00	

Vogel supposes it to contain ½ At. Aq. more.

Ammonio-cupric Oxalate. — Obtained by dissolving cupric oxalate in normal oxalate of ammonia, or cupric oxide in acid oxalate of ammonia. — Small rhombic laminæ, of a dark sky-blue colour and permanent in the air.

	Crystallized.		F. C. Vogel.	Graham.
NH^3	17	10·90		
CuO	40	25·64	25·0	25·27
C^4O^6	72	46·15	47·5	
3 HO	27	17·31		
$C^4(NH^4,Cu)O^8 + 2Aq$	156	100·00		

Permanent in the air below 100°; gives off 12 per cent of water above 100°, (11·46 p.c. = 2 At. according to Graham), but recovers it on exposure to the air; at a higher temperature, it gives off ammonia, becoming first brown, then copper-coloured, but retaining its crystalline form; if the air be then allowed to have access to it, vivid, lightning-like detonation takes place, and the copper appears to be oxidized. — The salt dissolves without decomposition in aqueous normal oxalate of ammonia, sparingly and with partial decomposition in water, cupric oxalate remaining undissolved and the excess of oxalate of ammonia being taken up by the water (F. C. Vogel). — When drops of the aqueous solution are placed upon bright metallic iron, several of them remain unaltered, while others instantly copper the iron; but the deposited copper becomes oxidated after a while by the action of the air, and redissolves, taking up oxalic acid and setting free ammonia, which prevents the coppering. If a number of rods of iron contained in separate glasses be immersed in the solution, some of them become coppered at the ordinary temperature, others only on the application of heat. The coppering of iron by this solution, when not exposed to the air, is very bright, dense, and permanent, and is therefore worthy of special recommendation (Wetzlar, *Schw.* 50, 93).

Potassio-cupric Oxalate. — Obtained in blue needles by Wenzel. — Produced by dissolving cupric carbonate in aqueous salt of sorrel, or cupric oxalate in normal oxalate of potash, or by mixing cupric sulphate with excess of normal oxalate of potash. The blue solution yields on cooling, first, greenish blue rhombohedrons permanent in the air, then blue, needle-shaped, six-sided, often flat prisms, bevelled with two faces resting on the broader lateral faces [perhaps as in *Fig.* 55], and quickly effloresing to a light blue mass (F. C. Vogel).

Rhombohedrons.			F. C. Vogel.
KO	47·2	26·64	26·08
CuO	40·0	22·57	22·50
C^4O^6	72·0	40·63	41·42
2 HO	18·0	10·16	10·00
$C^4KCuO^8 + 2Aq$	177·2	100·00	100·00

Needles.			F. C. Vogel.
KO	47·2	24·18	24·2
CuO	40·0	20·49	20·5
C^4O^6	72·0	36·84	37·3
4 HO	36·0	18·49	18·0
$C^4KCuO^8 + 4Aq$	195·2	100·00	100·0

Both kinds of crystals give off their water when heated; turn brown at a higher temperature, but without fusion; and leave carbonate of potash, together with cupric oxide or metallic copper, according as the air has access to them or not. To alcohol they give up, without dissolving, a portion of their water of crystallization. They dissolve sparingly in cold water, and in about 6 pts. of boiling water, leaving a residue of cupric oxalate, because the salt is soluble only in water previously containing normal oxalate of potash (F. C. Vogel).

Sodio-cupric Oxalate. — When oxalate of potash and soda is mixed with cupric sulphate, potassio-cupric oxalate in its two forms separates out first, and then this salt; the latter is also obtained by dissolving cupric oxalate in oxalate of soda. — Four-sided, often flat needles, of a

dark sky-blue colour, permanent in the air; when exposed to light, they first turn green, then black-brown, but without loss of weight. — When heated, the salt first gives off all its water, assumes a pale blue colour, and then decomposes, leaving a residue of carbonate of soda and metallic or oxidized copper. Dissolves sparingly in water, with separation of cupric oxalate; but aqueous oxalate of soda dissolves it without decomposition.

	Crystallized.			F. C. Vogel.
NaO	31·2	....	19·35	..... 19·02
CuO	40·0	....	24·81	..... 23·50
C^4O^6	72·0	....	44·67	..... 46·48
2 HO	18·0	....	11·17	..... 11·00
$C^4NaCuO^8 + 2Aq$	161·2	....	100·00	..... 100·00

Mercurous Oxalate. — Oxalic acid and oxalate of potash precipitate mercurous nitrate and sulphate. (Bergman). The salt is likewise obtained by mixing 1 pt. of mercurous oxide with 3 pts. oxalic acid and 2 pts. water, setting the mixture aside in a tolerably warm situation, and triturating it frequently; then diluting and washing with water. (Harff, *N. Br. Arch.* 5, 264). — White, loosely coherent powder, (Bergman), having a metallic taste (Harff). Blackens by exposure to light (Bergman) only while moist (Harff); the colour first changes to dirty yellow, then to dark brown (Burckhardt, *N. Br. Arch.* 11, 250). — It detonates slightly when suddenly heated (Klaproth), or when struck (Dulong). When suddenly heated in a glass tube, it detonates; when gradually heated, it merely decomposes with a hissing noise, especially if it has previously been rubbed to fine powder; if it be very gently heated, somewhat above 105°, it decomposes slowly and quietly but completely (Burckhardt). — The salt, when left for some time in contact with a large quantity of cold water, assumes a dirty yellow colour, which becomes blackish on boiling, and the filtrate contains a mixture of undecomposed mercurous salt with mercuric salt (H. Rose, *Pogg.* 53, 126). By long boiling with water, a basic and an acid salt are formed, the latter dissolving in the water (Harff). When heated with oil of vitriol, it gives off sulphurous and carbonic acid [and carbonic oxide?], and is converted, without blackening, into mercuric sulphate. It is blackened by ammonia, potash, and carbonate of ammonia (Harff, Burckhardt, Wittstein, *Repert.* 57, 43).

This salt is scarcely soluble in cold water, requiring according to Harff, 1000 pts. of water to dissolve it; according to Burckhardt, it is likewise insoluble, even in boiling water. Dissolves slightly in warm concentrated nitric and sulphuric acid, and separates out completely from both on cooling, or on the addition of water (Burckhardt). Dissolves somewhat more freely in aqueous oxalic acid than in water (Harff); according to Burckhardt, it is insoluble both in this acid and in dilute sulphuric and nitric acid, also in alcohol and ether.

	At 100°.			Burckhardt.	Harff.
$2Hg^2O$	416	....	82·21	..... 81·6	..... 83·73
C^4O^6	72	....	14·23		
2 HO	18	....	3·56		
$C^4Hg^4O^8 + 2Aq$	506	....	100·00		

Mercuric Oxalate. — Produced by digesting mercuric oxide with concentrated oxalic acid (Burckhardt), and by precipitating mercuric

acetate (Berzelius), or nitrate (Harff, Burckhardt), with oxalic acid, salt of sorrel, or normal oxalate of potash. Soft white powder, having a metallic taste (Harff, Burckhardt). Turns brown on exposure to light, but not so quickly as the mercurous salt (Burckhardt). Decomposes with a hissing noise when heated (Howard), being thereby resolved into mercury and carbonic acid; does not detonate by percussion (Burckhardt). Exhibits fiery decomposition when heated with potassium. With hot oil of vitriol it forms carbonic oxide, carbonic acid, and mercuric sulphate (Burckhardt). By continued boiling with water, it is resolved into a basic salt and an acid salt which dissolves. When immersed in ammonia, a portion of which it takes up, it remains white; but by immersion in potash, it is converted into yellow mercuric oxide (Harff). — It is perfectly insoluble in water and in aqueous oxalic acid (Burckhardt); insoluble in cold water, but slightly soluble in water containing oxalic acid (Harff). It dissolves with tolerable facility and without decomposition, in strong nitric acid, very sparingly in hot dilute nitric and sulphuric acid (Burckhardt). Dissolves sparingly in cold oil of vitriol, scarcely at all in alcohol, but is soluble in 416 pts. of ether (Burckhardt); perfectly insoluble in alcohol and ether (Burckhardt). Dissolves in aqueous hydrochlorate and nitrate of ammonia (Brett).

	Dried at 100°.			Burckhardt.	Harff.
$2\,HgO$	216	—	70·59	— 69	— 72·13
C^4O^4	72	—	23·53		
$2\,HO$	18	—	5·88		
$C^4Hg^2O^6+2Aq$	306	—	100·00		

Basic Ammonio-mercurous Oxalate? — By diffusing finely pounded mercurous oxalate in a bottle, and adding dilute ammonia, not in too great quantity, a black, tasteless powder is obtained, which must be washed and dried in the shade. It contains 90·13 p. c. of mercurous oxide. Moreover, when rubbed on the hand with water, it exhibits globules of mercury, and dissolves in acetic acid, leaving metallic mercury. When heated in a tube, it yields mercury, ammonia, and oxygen gas [not rather carbonic acid and water?]. Dissolves partially in nitric acid, forming ammonio-mercuric nitrate; yields calomel with hydrochloric acid; and gives off ammonia with potash. It is soluble in water, alcohol, and ether (Harff, *N. Br. Arch.* 5, 266).

Ammonio-mercuric Oxalate? — *a. Basic?* Prepared in the same manner from mercurous oxalate. Loose, white powder, having a metallic taste. Contains 82·98 p. c. mercuric oxide. Turns yellow when heated in a glass tube, or boiled continuously with water, or moistened with a small quantity of oil of vitriol. Similarly with potash, giving off ammonia at the same time. Dissolves readily in strong hydrochloric acid, forming a solution which gives a white precipitate with potash. Dissolves sparingly in cold, more freely in hot nitric acid, in 416 pts. of cold water, and in 476 pts. of alcohol, but is insoluble in ether (Harff).

b. Normal? — When mercuric oxalate (or mercurous oxalate, in which case metallic mercury separates out), is digested with aqueous ammonia; or better, when mercuric oxalate is digested with aqueous normal oxalate of ammonia, and one of these liquids is left to evaporate slowly after being filtered, white shining laminæ are obtained, having a metallic taste, and quickly turning yellow on exposure to light. They [illegible]dt when heated; give off ammoniacal fumes; and are finally resolved,

with strong detonation, into mercury and carbonic acid. With potash they evolve ammonia, and yield mercuric oxide. They dissolve in water with partial decomposition, mercuric oxalate remaining undissolved (Burckhardt, *N. Br. Arch.* 11, 256).

Potassio-mercurous Oxalate? — An aqueous solution of salt of sorrel saturated with mercurous oxide yields rhombic prisms (Wenzel). When mercurous oxide is digested for 24 hours with an equal weight of salt of sorrel and with water, the mixture being frequently shaken, the filtrate, when repeatedly evaporated and cooled, yields nothing but crystals of salt of sorrel; but the last mother-liquor yields a small quantity of white, metallic flavoured prisms, which must be washed and recrystallized. They are resolved by heat into sublimed mercury and a residue of carbonate of potash. They are blackened by potash or ammonia. Dissolve gradually in warm nitric or sulphuric acid. Dissolve readily in water, but are insoluble in alcohol and ether: hydrochloric acid added to the aqueous solution throws down calomel (Harff). — According to Burckhardt, this salt cannot be formed, inasmuch as neither mercurous oxide nor mercurous oxalate dissolves in salt of sorrel, or in normal oxalate of potash. Neither, according to the same authority, does mercuric oxalate form a double salt with potash.

Oxalate of Silver. — Oxalic acid added to nitrate or sulphate of silver, throws down a white powder, which does not redden litmus, but turns brown on exposure to light. (Bergman.) It detonates slightly when forcibly struck; even after being dried as completely as possible, it yields water when heated, as well as silver and carbonic acid (Dulong). The quantity of water thus retained is 2 p.c. = $\frac{1}{8}$ At. (Hausmann & Löwenthal). The salt is decomposed by heat, with a hissing noise, becoming at the same time strongly electrical (Döbereiner, I. 340). — Heated to 100° in a current of hydrogen gas, it assumes a light brownish-yellow colour, perhaps by partial conversion into oxalate of suboxide of silver; at 140° it turns brown, and then immediately detonates with violence. (Wöhler, *Ann. Pharm.* 30, 4.) When immersed in water, it is not decomposed by heat, but partially by exposure to sunshine, into carbonic acid and silver. Döbereiner, *Schw.* 62, 95.) — The salt is scarcely soluble in water, but dissolves in nitric acid. (Bergman.) It dissolves in aqueous caustic ammonia and carbonate of ammonia, and when heated with solution of sal-ammoniac (Brett), or sulphate or nitrate of ammonia (Wittstein), it forms a clear solution which becomes turbid as it cools.

	Anhydrous.		Hausmann & Löwenthal.
2 AgO	232	76·31	76·83
C^4O^6	72	23·69	23·17
$C^4Ag^2O^8$	304	100·00	100·00

The 2 p.c. water not driven off by heat is regarded as not essential to the constitution of the salt (Hausmann & Löwenthal).

Potassio-silver Oxalate. — The solution of silver-oxide in aqueous salt of sorrel yields easily soluble rhomboïdal crystals, which are permanent in the air (Wenzel).

Argento-chromic Oxalate. — $3(AgO,C^2O^3) + Cr^2O^3,3C^2O^3 + 9Aq$. [$= C^{12}Ag^3Cr^2O^{24} + 9Aq$]. — A mixture of the solutions of nitrate of silver and blue potassio-chromic oxalate gradually deposits dark blue shining needles,

which are obtained in a state of greater purity by solution in ot water and cooling. They contain 11·15 per cent. of water, part of which they give up on exposure to the air, assuming a greyish colour; at 120° they still retain 1 At. water. At a higher temperature, they burn with slight explosion, but without projection. They dissolve with blue colour in more than 65 pts of water at 15°, and in 9 pts. of boiling water (Berlin).

Oxalate of Gold appears to be incapable of existing (p. 119). — The following additional facts are stated by Hensmans (*Repertoire de Chemie*, 1, 312): Chloride of gold mixed with aqueous salt of sorrel is not reduced, even by heat; the yellow mixture loses its colour as it cools, and deposits a large number of yellow needles, which dissolve readily in water, forming a solution which gives off carbonic acid when heated, and forms a yellow precipitate.

Platinous Oxalate. — Warm aqueous oxalic acid dissolves platinate of soda, giving off carbonic acid, and forming a dark liquid, which, as it cools, first becomes green, then dark blue, and afterwards deposits small dark, copper-coloured needles of platinous oxalate, which explode when heated, without appearance of fire, and yield water and carbonic acid. The pale blue mother-liquor becomes yellow when diluted with water, and dark blue again when evaporated (Döbereiner, *Pogg.* 28, 182).

Platinic Oxalate. — The precipitate formed by soda in a solution of bichloride of platinum dissolves with yellow colour in oxalic acid, and yields yellow crystals (Bergman).

Ammonio-chloroplatinous Oxalate. — *Ammonio-oxalate of Oxychloride of Platinum.* — Oxalic acid added, either in the free state or in combination with an alkali, to an aqueous solution of ammonio-sulphate or nitrate of oxychloride of platinum (VI, 310, 311), throws down a white granular salt insoluble in water, and reconverted into the sulphate or nitrate by an excess of sulphuric or nitric acid (Gros, *Ann. Pharm.* 27, 252).

					Gros.
4 N	56·0	....	13·18	.....	13·05
12 H	12·0	....	2·83	.....	2·99
2 Pt	198·0	....	46·61	.....	45·79
2 Cl	70·8	....	16·66	.....	16·65
4 C	24·0	....	5·65	.....	5·61
8 O	64·0	....	15·07	.....	15·91
$4NH^3 + C^4(PtCl)^2O^8$	424·8	....	100·00	.....	100·00

¶ According to Gerhardt's formulæ, this salt is the *Bichlorhydroxalate of Diplatinamine* $= \left.\begin{matrix} C^2H^2O^4 \\ 2ClH \end{matrix}\right\} 2N^2H^4\,pt^2$.

Ammonio-oxyplatinous Oxalate. — When oxalate of ammonia is added to a solution of neutral nitrate of platinamine (ammonio-nitrate of platinic oxide, VI, 311, 315), a light yellow crystalline precipitate is formed, which when redissolved in boiling water, yields laminæ of the same colour (Gerhardt, *Compt. rend. trav. Chim.* 1850, 283).

					Gerhardt.
2 N	28	....	7·53	.....	7·93
10 H	10	....	2·69	.....	2·92
2 Pt	198	....	53·22	.....	53·16
4 C	24	....	6·45	.....	6·19
14 O	112	....	30·11	.....	29·80
$2NH^3 + C^4(PtO)^2O^8 + 4Aq$	372	....	100·00	.....	100·00

This is Gerhardt's *Neutral Oxalate of Platinamine* $= C^2H^2O^4, 2NHpt^2 + 3Aq$. ¶

Palladious Oxalate. — Alkaline oxalates form a light yellow precipitate with palladious nitrate (Berzelius).

Ammonio-palladious Oxalate. — 1. Produced by mixing the colourless ammoniacal solution of any palladious salt with oxalic acid. — 2. By dissolving recently precipitated hydrate or carbonate of palladious oxide in acid oxalate of ammonia. — The double salt crystallizes, with 2 At. water of crystallization, in short rhombic prisms of a fine bronze-yellow colour, which give off 11·57 per cent of water when heated; and with 8 At. water, in long needles of the same colour, which give off 30 per cent of water when heated. — Both salts, when burnt with oxide of copper, yield exactly 4 vol. carbonic acid to 1 vol. nitrogen (Kane, *Phil. Trans.* 1842, 297).

Prisms.				Kane.
NH^3	17·0	....	9·59	
Pd	53·3	....	30·06	..... 30·20
O	8·0	....	4·51	
C^4O^6	72·0	....	40·61	
3 HO	27·0	....	15·23	
$C^4(NH^4,Pd)O^8 + 2Aq$	177·3	....	100·00	

Needles.				Kane.
NH^3	17·0	....	7·35	
Pd	53·3	....	23·04	..... 23·13
O	8·0	....	3·46	
C^4O^6	72·0	....	31·13	
9 HO	81·0	....	35·02	
$C^4(NH^4,Pd)O^8 + 8Aq$	231·3	....	100·00	

Oxalate of Urea. — Precipitated in the crystalline form, on mixing the concentrated aqueous solutions of oxalic acid and urea (Prout). For the preparation, *vid.* VII. 372.

Long thin laminæ having a very pure acid taste (Berzelius). Large rectangular tables (Morin).

The compound when heated melts, boils, and splits up, like its constituents, into carbonate of ammonia and cyanuric acid on the one hand, and carbonic oxide and carbonic acid on the other. If it is contaminated with oxalate of potash, it gives off a small quantity of hydrocyanate of ammonia, and leaves charcoal mixed with [carbonate of?] potash (Berzelius). — The crystals became opaque at 120°, and give off 14·3 per cent (4 At.) water. The residue decomposes at a stronger heat before it begins to melt (Marchand). These hydrated crystals have not been obtained by any one else. The air-dried crystals give off at 120° only 0·14 to 0·57 water, merely hygroscopic water therefore (Werther, *J. pr. Chem.* 35, 484). — The crystals fuse and blacken slightly when heated, yielding, first water and a small quantity of gas which smells of ammonia, then white fumes which form a sublimate of oxamide (Morin).

Oxalate of urea dissolves in 23 pts. of water at 15°, and in a much smaller quantity of hot water; the cold saturated solution is partially precipitated by excess of oxalic acid (Berzelius). It dissolves in 60·5 pts. of alcohol of sp. gr. 0·833 at 16°, and in a somewhat smaller quantity of hot alcohol (Berzelius). It appears to unite with normal alkaline oxalates, forming double salts which are soluble in alcohol (Berzelius, *Lehrb.*).

	At [illegible]		Regnault.
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	4·79
[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	100·00	

[illegible]	At [illegible]		Marchand.	Werther.
[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	33·5	33·7
[illegible]	[illegible]	100·00		

Regnault (*Ann. Pharm.* [illegible]); Marchand (*J. pr. Chem.* 34, 248; 35, 485). — The obviously incorrect analyses of Morin (*Ann. Chim. Phys.* [illegible]) are not given here. His experiments on urea mentioned in the same paper led him to the very improbable assumption of a hypothetical radical [illegible], which he supposed to be composed, like amidogen, of NH^2.

¶ *Oxalate of Methylamine.* — *a. Neutral.* $2C^2H^3N.C^4H^2O^8 = C^6(C^2H^3N)^2O^8$. — When oxalic acid is saturated with methylamine, a solution is obtained, which may be evaporated to a syrupy consistence, but does not crystallize readily. 0·384 grm. of this substance precipitated with chloride of calcium gave 0·3846 grm. of oxalate of lime, corresponding to 0·2289 grm., or 59·6 per cent of C^2HO^8; the preceding formula requires 59·2 per cent. — This salt, when subjected to dry distillation, is resolved into water and *methyloxamide*.

$$C^6H^{12}N^2O^8 = \underbrace{C^6H^8N^2O^6}_{\text{Methyloxamide.}} + 4HO.$$

This transformation takes place more readily than the corresponding transformation of oxalate of ammonia into water and oxamide, because methyloxamide is more volatile than oxamide (Wurtz).

b. Acid. $C^6H.C^2H^3N.O^8$. — Obtained by mixing the salt *a* with a quantity of oxalic acid equal to that which it already contains. Crystallizes more readily than the neutral salt, and is deposited from its alcoholic solution in the form of small laminæ. Heated to 160°, it is resolved into 2 At. water and *methyloxamic acid*, $C^6H^3NO^8$ (Wurtz, *N. Ann. Chim. Phys.* 30, 464).

Oxalate of Ethylamine. — Obtained by saturating ethylamine with oxalic acid. The solution, when evaporated, yields the salt in right rhomboidal prisms with truncated summits.

			Wurtz.
12 C	72	40·00	40·28
16 H	16	8·88	9·01
2 N	28	15·55	15·58
8 O	64	35·57	35·13
$C^4(C^4H^8N)^2O^8$	180	100·00	100·00

This salt is readily decomposed by heat in the same manner as oxalate of ammonia, giving off 2 At. water, and forming *Ethyloxamide:*

$$C^{12}H^{16}N^2O^8 = \underbrace{C^{12}H^{12}N^2O^8}_{\text{Ethyloxamide.}} + 4HO.$$

When it is mixed with excess of oxalic acid, and the mixture fused for some time over the oil-bath at 180°, a small quantity of *Ethyloxamic acid* is formed (Wurtz, *N. Ann. Chim. Phys.* 30, 489). ¶.

Aqueous Oxalic acid with Prussian blue. — The *blue ink* invented by Stephan and Nash. — 6 parts of pure prussian blue, triturated with 1 or 2 pts. of oxalic acid and a small quantity of cold water, forms a soft paste (Mohr), and with 64 pts. water, a dark blue syrup, which by addition of a larger quantity of cold water, is converted into a clear, thin, dark blue liquid (Karmarsch, *J. pr. Chem.* 20, 175). Prussian blue prepared from ferrocyanide of potassium and ferric sulphate, and washed with water by decantation, may be used for this purpose (Mohr, *Ann. Pharm.* 34, 348); or commercial Paris blue, purified if necessary, by treating it with hydrochloric acid and afterwards with water (Stephan & Nash). — The solubility of prussian blue in oxalic acid is increased by previous purification with strong hydrochloric or sulphuric acid (Stephan & Nash). — 6 parts of prussian blue, purified with oxalic acid, form with 1 pt. of oxalic acid and 256 parts of water, a solution which passes completely through the filter. If the prussian blue has been previously mixed with a sufficient quantity of oil of vitriol to turn it white, and the sulphuric acid has then been dissolved out by water, 1 part of oxalic acid is sufficient to render 8 parts of the prussian blue completely soluble in 256 parts of water. Neither of these two solutions yields any deposit on exposure to the air, as is the case with those which are made with prussian blue not previously purified by acids (Karmarsch). — With prussian blue not so prepared, it is best to use 2 pts. of oxalic acid with 6 pts. of prussian blue; a still larger quantity of oxalic acid is useless, and causes precipitation; those solutions which contain the smallest proportion of oxalic acid are also least subject to decomposition (Karmarsch). — With less than 100 parts of water to 1 pt. of prussian blue, the solution is not complete; if, for example, the syrup obtained with 1 pt. oxalic acid, 6 pts. prussian blue, and 64 pts. water be diluted, after 24 hours, with only 64 pts. water, and filtered, a dark blue liquid passes through, and there remains on the filter a thick blue magma, which dissolves completely in a larger quantity of water, forming a blue liquid. With 1 pt. oxalic acid to 2 pts. prussian blue, a smaller quantity of water suffices for solution (Karmarsch).

The filtered solution, when evaporated, leaves a syrup which dries up to a dark blue earthy mass, which has a coppery lustre in parts, is mixed with colourless crystals of oxalic acid, but redissolves in water. If, however, the solution has been prepared with 2 pts. of oxalic acid and 1 pt. of prussian blue, the whole of the blue separates completely as the liquid evaporates; and the decanted colourless liquid, when further evaporated, yields crystals of oxalic acid, mixed with a few brown-yellow flakes of iron-salt, a proof that the acid has removed a portion of the iron (Karmarsch). — If the blue liquid is diluted with too much water, it becomes decolorized after standing for some weeks, and forms a blue precipitate; but a less dilute solution, *e. g.*, 1 pt. oxalic acid, 6 pts. prussian blue, and 256 pts. of water, does not decompose, either by long standing, or when heated (L. A. Buchner, *Repert.* 72, 136). According to Mohr, on the other hand, the solution yields no deposit even when very much diluted.

The blue liquid becomes brown-red when mixed with carbonate of potash, but does not deposit ferric oxide till boiled, the quantity then deposited amounting to $\frac{2}{3}$ of that which was contained in the dissolved

prussian blue; the yellow liquid filtered from the ferric oxide, yields a blue precipitate with hydrochloric acid (Williamson, *Ann. Pharm.* 57, 242).

If the blue liquid is to be used as ink, a quantity of shellac must be boiled with an equal weight of crude potash and with water, the solution mixed with a small quantity of lamp-black, and a portion of the mixture added to the blue liquid (Stephan & Nash).

Hydrated Oxalic acid dissolves in 2·5 pts. of cold highly rectified *spirit*, and in 1·8 parts of the same liquid at a boiling heat. It is but sparingly soluble in *ether*.

Conjugated Compounds of the Secondary Nucleus $C^4H^3O^2$.

Oxalate of Methyl. $C^6H^6O^8 = 2C^2H^3O + C^4O^6$.

Dumas & Peligot (1835). *Ann. Chim. Phys.* 58, 44; also *Ann. Pharm.* 15, 32.

Weidmann & Schweizer. *Pogg.* 43, 602; *J. pr. Chem.* 23, 7.

Methylic Oxalate, Kleeholzäther, kleesaures Methylen, oxalsaures Methyloxyd, Oxalate de Methylène, Oxalformester.

Preparation. 1. By distilling a mixture of equal parts of wood-spirit, oxalic acid, and oil of vitriol. The first portion of the distillate deposits crystals of the compound when left to evaporate; the last portion contains so large a quantity that it solidifies in the crystalline form on cooling. By adding to the cooled residue a quantity of alcohol equal to the first portion, and distilling again, an additional quantity of methylic oxalate may be obtained. — The crystals, after being drained, are fused and then rectified over dry oxide of lead to remove free oxalic acid (Dumas & Péligot). — 2. By distilling 1 pt. of wood-spirit with 1 pt. of binoxalate of potash and 2 pts. of oil of vitriol. Wood-spirit passes over first, and then the methylic oxalate sublimes in crystals without any evolution of sulphurous acid; but as soon as its formation ceases, sulphurous and acetic acid pass over, together with a small quantity of methol, and sometimes also sulphomethylic acid. The crystals are pressed between paper and sublimed at a gentle heat over oxide of lead (Weidmann & Schweizer). — ¶. Wöhler (*Ann. Pharm.* 81, 376) mixes 1 pt. of wood-spirit, gradually so as to avoid rise of temperature, with 1 pt. of oil of vitriol, and distils the mixture with 2 parts of binoxalate of potash (it should be left for 24 hours before distilling), whereupon a combustible liquid passes over first, containing a certain quantity of methylic oxalate, which may be separated by evaporation, and afterwards methylic oxalate which solidifies in the neck of the retort; the latter is collected apart, pressed between bibulous paper and purified by standing over oil of vitriol, or by keeping it for some time in the melted state. ¶. — 3. Methylic oxalate may likewise be obtained by distilling wood-spirit with oxalic acid alone, and cohobating the product (Weidmann & Schweizer). — Also by treating perchlorinated methylic oxalate, $C^6Cl^6O^8$, with wood-spirit (Cahours).

Properties. Colourless rhombic crystals. Melts at 51°, boils at 160°, (bar. at 0·761 met.); smells like oxalic ether (Dumas & Péligot).

			Dum. & Pél.	Weidm. & Schw.
8 C	48	40·68	41·08	41·08
6 H	6	5·09	5·28	5·18
8 O	64	54·23	53·64	53·74
$C^8H^6O^8$	118	100·00	100·00	100·00

Decompositions. 1. Chlorine gas, with the aid of heat or sunshine, slowly converts methylic oxalate (with formation of hydrochloric acid) into chlorinated methylic oxalate, $C^8H^2Cl^4O^8$, and afterwards into perchlorinated methylic oxalate, $C^8Cl^6O^8$. (Malaguti, *Ann. Chim. Phys.* 70, 383; *Compt. rend.* 23, 1071). — 2. Methylic oxalate dissolves in water, but when dissolved is quickly decomposed, especially if heated, into wood-spirit and oxalic acid, so that the solution, even when recently prepared, precipitates lime-water (Dumas & Péligot). It first dissolves in water without decomposition; but in the course of a few hours, is resolved into oxalic acid and methol, without yielding a trace of wood-spirit. This methol is an oil, nearly as heavy as water; smells more powerfully aromatic than the methol obtained from methylic sulphate; and contains 80·19 p. c. carbon, 13·98 hydrogen, and 5·83 oxygen; it is, therefore, $C^{20}H^{22}O$. (Weidmann & Schweizer.) — 3. Aqueous solutions of the fixed alkalis immediately decompose methylic oxalate into wood-spirit and an alkaline oxalate; but anhydrous oxide of lead exerts no decomposing action. (Dumas & Péligot):

$$C^8H^6O^8 + 2KO + 2HO = C^4K^2O^8 + 2C^2H^4O^2.$$

When methylic oxalate is very carefully decomposed by dilute potash, wood-spirit is actually obtained. (Weidmann & Schweizer, *J. pr. Chem.* 23, 7.) Löwig, in a former experiment (*Pogg.* 42, 409), in which he distilled several ounces of methylic oxalate with potash-ley, did not obtain a trace of wood-spirit; but more recently (*Organ. Verb.*) he admits the resolution of the compound into alcohol and oxalate of potash. — 4. Aqueous ammonia converts methylic oxalate into wood-spirit and oxamide (Dumas & Péligot):

$$2C^2H^3O,C^4O^6 + 2NH^3 = 2C^2H^4O^2 + C^4N^2H^4O^4.$$

5. Dry ammoniacal gas converts it into wood-spirit and oxamethylane. (Dumas & Péligot.)

$$2C^2H^3O,C^4O^6 + NH^3 = C^2H^4O^2 + C^6NH^5O^6.$$

Chloromethylic Oxalate. $C^8H^2Cl^4O^8 = 2C^2HC^2O,C^4O^6$.

Malaguti (1839). *Ann. Chim. Phys.* 70, 383; also *Ann. Pharm.* 32, 49; also *J. pr. Chem.* 18, 62.

Chlorhaltiges kleesaures Methylen, Oxalate de Methylène chloruré, Chloroxalformester.

When dry chlorine gas is passed through fused methylic oxalate not exposed to the direct rays of the sun, a slow action takes place, and a small portion of the compound is converted, in the course of 14 days, into a liquid which does not solidify at ordinary temperatures. On decanting this liquid, and decomposing the methylic oxalate still contained in it by continuing the passage of the chlorine till a sample of the liquid dissolves completely in water without effervescence, then decoloriz-

ing the yellow fuming liquid by the application of a gentle heat, and partially distilling it with frequent change of receiver, a mixture of oxalic acid, methylic oxalate, and a small portion of chloromethylic oxalate remain behind, and distillates are obtained, some of which when dissolved in water, give off carbonic oxide gas alone, others a mixture of carbonic oxide and carbonic acid. The former must be regarded as the purer chloromethylic oxalate; the latter, in which the proportion of carbonic acid evolved amounts to $\frac{1}{15}$ of the carbonic oxide, must be rejected.

Transparent, colourless liquid.

				Malaguti.
8 C	48·0	18·78		17·06
2 H	2·0	0·78		
4 Cl	141·6	55·40		49·65
8 O	64·0	25·04		
$C^8H^2Cl^4O^8$	255·6	100·00		

In water it instantly disappears, being converted into oxalic acid, hydrochloric acid, and carbonic oxide, which escapes with effervescence:

$$C^8H^2Cl^4O^8 + 4HO = C^4H^2O^8 + 4CO + 4HCl.$$

In this decomposition, 100 pts. of chlormethylic oxalate yield 38·82 pts. hypothetical anhydrous oxalic acid, and a quantity of carbonic oxide containing 4·12 pts. of carbon.—In damp air, it is quickly converted into crystallized oxalic acid (Malaguti).

Perchloromethylic Oxalate.

A. Cahours (1846). *N. Ann. Chim. Phys.* 19, 343; also *J. pr. Chem.* 40, 425; abstr. *Compt. rend.* 23, 1071.

Perchloroxalsaurer Methyläther, Oxalate de Methylène perchloré; Perchloroxalformester.

Obtained by introducing perfectly dry methylic oxalate into bottles filled with dry chlorine gas and exposing them to sunshine. The brisk action which takes place at first soon diminishes. After several days' exposure to sunshine, when the colour of the remaining free chlorine no longer diminishes, the methylic oxalate is completely converted into crystals of the chlorine-compound.

Snow-white, nacreous crystalline laminæ, which melt at a gentle heat, and sublime partly undecomposed at a stronger heat; they have a very powerful odour, like that of phosgene.

				Cahours.
8 C	48·0	14·79		14·69
6 Cl	212·4	65·48		65·06
8 O	64·0	19·73		20·25
$C^8Cl^6O^8$	324·4	100·00		100·00

This compound is resolved, partially by simple sublimation, but completely when its vapour is passed through a glass tube heated to a temperature between 300° and 400°, into phosgene and carbonic oxide:

$$C^8Cl^6O^8 = 6CClO + 2CO.$$

In caustic potash-solution, it disappears with violent action and formation of oxalate and carbonate of potash and chloride of potassium:

$$C^8Cl^6O^8 + 12KO = C^4K^2O^8 + 4(KO,CO^2) + 6KCl.$$

Soda-solution and baryta-water exert a similar action. — Ammoniacal gas acts violently upon it, forming carbamide = CNH^2O (II, 481), and sal-ammoniac.

[According to what equation?]—A small quantity of brown matter is formed at the same time.

With wood-spirit, it is decomposed, with great heat and intumescence, into hydrochloric acid gas, which escapes, methylic oxalate, amounting to $\frac{1}{3}$ of the perchloromethylic oxalate, and chloromethylic formiate (VII, 309). If therefore water be added to the cooled mixture, a heavy oil sinks to the bottom, which, when distilled, gives off chloromethylic formiate between 78° and 82°, and afterwards methylic oxalate at 162°:

$$C^8Cl^6O^8 + 4C^2H^4O^2 = 4HCl + C^8H^6O^8 + 2C^4H^3ClO^4.$$

Alcohol added in small portions to methylic oxalate, produces great rise of temperature and evolution of hydrochloric acid gas, while oxalic ether and chlorovinic formiate remain behind. When the addition of fresh alcohol no longer produces effervescence, the liquid is left to cool and mixed with a large quantity of water, whereby an oily mixture is thrown down, consisting of the two ethers, which may be separated by distillation:

$$C^8Cl^6O^8 + 4C^4H^6O^2 = 4HCl + C^{12}H^{10}O^8 + 2C^6H^5ClO^4.$$

In a similar manner, fusel-oil and perchloromethylic formiate mixed together, become heated, give off hydrochloric acid, and form amylic oxalate and chloramylic formiate (Cahours):

$$C^8Cl^6O^8 + 4C^{10}H^{12}O^2 = 4HCl + C^{24}H^{22}O^8 + 2C^{12}H^{11}ClO^4.$$

Oxamethylane. $C^8NH^5O^6 = C^2H^3Ad,C^4O^6$.

Dumas & Péligot (1835). *Ann. Chim. Phys.* 58, 60.

Oxamethylan, Oxalformamester.

Dry ammoniacal gas is passed, to saturation, over heated methylic oxalate, till in fact, the mass, which is liquid at first, solidifies without alteration of temperature to a white crystalline mass:

$$2C^2H^3O,C^4O^6 + NH^3 = C^6H^5NO^6 + C^2H^4O^2.$$

Although the absorption of the ammonia is attended with some rise of temperature, it is nevertheless necessary, for complete transformation, to apply heat from without, so as to keep the mass in the liquid state (Dumas & Péligot).

White crystalline mass (Dumas & Péligot). Crystallizes from the alcoholic solution by evaporation in pearly cubes (Liebig). Soluble in boiling alcohol.

			Dumas & Péligot.
6 C	36	34·95	35·0
5 H	5	4·86	5·0
N	14	13·59	13·9
6 O	48	46·60	46·1
C^2H^3Ad,C^4O^6	103	100·00	100·0

May be regarded as a compound of oxide of methyl with oxamic acid (VII, 220.) When it is boiled with water, and ammonia added by drops, so as to neutralize the acid as soon as it is set free, till the compound is completely decomposed, the liquid is found to contain nothing but oxamate of ammonia (Balard, *N. Ann. Chim. Phys.* 4, 101; also *Ann. Pharm.* 42, 203; also *J. pr. Chem.* 25, 84).

Oxalate of Ethyl. $C^{12}H^{10}O^8=2C^4H^5O,C^4O^4$.

Bergman. *Opuscula*, 1, 256.
Thénard. *Mém. de la Soc. d'Arcueil*, 2, 11.
Bauhof. *Schw.* 19, 308.
J. Dumas & P. Boullay. *J. Pharm.* 14, 113; also *Schw.* 52, 337 and 432.
Dumas. *Ann. Chim. Phys.* 54, 237; also *Ann. Pharm.* 10, 288.

Ethylic Oxalate, Vinic Oxalate, Oxalic Ether, Kleenaphtha, Kleeäther, Oxaläther, Kleesaures oder oxalsaures Aethyloxyd, Oxal-vinester, Ether oxalique, Oxalate d'Oxide d'Ethyle, Oxalate éthylique. — Discovered by Bergman; more minutely investigated by Thénard, Bauhof, Dumas & Boullay.

Formed by heating oxalic acid with alcohol (Bauhof); more readily in presence of sulphuric acid (Thénard).

Produced also, together with chlorovinic formiate and hydrochloric acid, in the decomposition of perchloromethylic oxalate by alcohol. (Cahours, *Ann. Chim. Phys.* 19, 348). — ¶. Also in the preparation of crude aldehyde, by distilling a mixture of equal parts of peroxide of manganese, sulphuric acid, and spirit of 20 per cent (C. Schmidt, *Ann. Pharm.* 83, 330). ¶

Preparation. 1. A mixture of 1 pt. oxalic acid and 8 or 10 pts. of 96 per cent alcohol is heated for some days, and then distilled, the distillate being poured back again six times or more, till the residue no longer crystallizes, but assumes the form of an oily liquid, which may then be distilled over without residue as oxalic ether; for this last distillation the receiver should be changed; the free acid is separated by agitation with carbonate of lime (Bauhof). A good mode of proceeding is to mix dehydrated oxalic acid with three times its weight of absolute alcohol, and heat the mixture on the water-bath for 8 days, in a flask provided with an upright tube 3 ft. long and surrounded with damp paper, so that the alcohol may condense in it and run back again; then attach to the flask a bent tube *b* (*App.* 51), and distil, whereupon alcohol passes over first, and afterwards the oxalic ether, which must be collected in a separate receiver (Gm.). — Bergman, by distilling equal parts of oxalic acid and alchohol, obtained: first alcohol; then a distillate

from which lime-water separated an ether lighter than water, and burning with difficulty; and lastly, a heavy oil. — 2. One part of effloresced oxalic acid and 6 pts. of absolute alcohol are distilled in a retort provided with a thermometer, till the boiling point rises to 140°; the distillate poured back, and redistilled till the boiling point rises to 160°; the residue, consisting chiefly of oxalic ether, agitated several times with water to remove free acid; and rectified over oxide of lead: the portion which passes over above 180° is pure oxalic ether, amounting to 1 pt. for every 2 pts. of acid (Mitscherlich, *Lehrb.*). — 3. Oxalic acid is heated in a tubulated retort till it begins to give off white fumes (to 180°—200°, according to Chancel), and alcohol dropped in through the tubulus. Oxalic ether then passes over in large quantity mixed with a little undecomposed alcohol. (Gaultier de Claubry, *Rev. scientif.* 9, 363; also *Ann. Pharm.* 43, 127). — 4. Alcohol quickly heated with oxalic acid to 200° in a narrow glass tube with thin sides, immediately forms oxalic ether (Guérin, *ibid.*). — 5. A mixture of 15 pts. oxalic acid, 18 pts. alcohol, and 5 pts. oil of vitriol is distilled till a small quantity of vinic ether is formed. The brown acid residue in the retort, when mixed with water, deposits oxalic ether, which must be washed with aqueous potash and cold water (Thénard). The quantity thus obtained is but small (Dumas & Boullay). — 6. A mixture of 1 pt. binoxalate of potash, 1 pt. alcohol, and 2 pts. oil of vitriol, is distilled till the retort no longer contains alcohol. The first portion of the distillate consists of alcohol; then comes ether, and an oily liquid which sinks to the bottom and contains the greater part of the oxalic ether. The alcohol is poured off (if poured back into the retort once or twice, it yields more oxalic ether, and when mixed with water, deposits a still further quantity); the heavy liquid shaken up in a cylindrical vessel with water; exposed to the air till the vinic ether, which often makes it lighter than water, is evaporated; boiled with litharge in a short-necked flask till the boiling point, which is at first between 90° and 100°, has risen to 183° or 184°, whereby it is freed from acid, as well as from alcohol, ether, and water; then decanted; and the ether distilled off in a very dry retort (Dumas & Boullay). — Oxalic ether thus prepared, is at first contaminated with a large quantity of sulphovinate of wine-oil, which may however be completely removed by boiling for a sufficient time with litharge. Its presence may be recognized by throwing a piece of potassium upon the oxalic ether, and setting fire to the liquid; the charred mass becomes red hot, and leaves a residue, which, when dissolved in water and filtered, precipitates chloride of barium, and gives off sulphuretted hydrogen when mixed with hydrochloric acid.

Properties. Colourless after rectification; otherwise yellowish (Thénard); brownish yellow (Bauhof). Oily. Sp. gr. 1·0929 at 7·5°. Boils between 183° and 184°, the barometer standing at 076°. Vapour-density = 5·087 (Dumas & Boullay); = 5·10 (Cahours). Inodorous (Thénard); smells like wine-oil and fusel-oil (Bauhof); has an aromatic but slightly alliaceous odour (Dumas & Boullay). Taste slightly astringent (Thénard); very disagreeable, bitter and astringent (Bauhof):

			Dum. & Boull.	Dumas.	Cahours.
12 C	72	49·31	49·28	49·4	49·00
10 H	10	6·85	6·79	6·8	6·77
8 O	64	43·84	43·93	43·8	44·23
$C^{12}H^{10}O^8$	146	100·00	100·00	100·0	100·00

	Vol.	Density.
C-vapour	12	4·9920
H-gas	10	0·6930
O-gas	4	4·4372
Vapour of Oxalic ether	2	10·1222
	1	5·0611

Decompositions. 1. Oxalic ether is decomposed by *Chlorine*, with the aid of heat and sunshine, but not otherwise, yielding perchloroxalic ether ($C^{12}Cl^{10}O^8$) and hydrochloric acid (Malaguti, *Ann. Chim Phys.* 74, 299; *comp.* Laurent, *Ann. Chim. Phys.* 66, 317). — 2. In contact with *Water*, oxalic ether is resolved slowly in the cold, quickly with the aid of heat, into alcohol and oxalic acid. On distilling it with water, the decomposition takes place immediately (Bauhof); when the two liquids are merely mixed in the cold, it takes place slowly; in vessels which do not close well, the mere entrance of moist air gives rise to a separation of oxalic acid. — 3. *Aqueous solutions of the fixed alkalis*, such as potash-ley (Thénard), or baryta-water (Bauhof), produce this decomposition with greater rapidity. 100 pts. of oxalic ether yield, with potash, 62·18 pts. of absolute alcohol and a quantity of oxalate of potash containing 49·98 pts. of hypothetical anhydrous oxalic acid; this shows an excess of 11·16 pts., proceeding from hydrogen and oxygen taken up during the reproduction of the alcohol (Dumas & Boullay). For the reaction of oxalic ether with an insufficient quantity of potash, see *Oxalovinic acid*, p. 183. — 4. Oxalic ether added to *a mixture of lime and hydrate of potash* contained in a retort, sinks into the powder, producing great heat, and probably forming oxalate of potash and ethylate of potassium; the mass, when heated, gives off hydrogen, and afterwards contains acetic acid (proceeding from the alcohol) and carbonic acid (from the oxalic acid) (Dumas & Stas, *Ann. Chim. Phys.* 73, 152; also *Ann. Pharm.* 35, 161; also *J. pr. Chem.* 21, 373). — 5. *Aqueous Ammonia* decomposes oxalic ether, yielding alcohol and oxamide (Liebig, *Pogg.* 31, 334):

$$2C^4H^5O,C^4O^6 + 2NH^3 = 2C^4H^6O^2 + C^4N^2H^4O^4.$$

When oxalic ether is shaken up with excess of ammonia, the drops of ether which diffuse through the liquid solidify in white masses retaining the spherical form. (Dumas.) — Bauhof, who first observed the formation of oxamide in this manner, regarded it as a compound of oxalic ether with ammonia. — 6. *Dry ammoniacal gas* passed through oxalic ether is absorbed, with evolution of heat, and decomposes the ether into alcohol and oxamethane; by continuing the passage of the gas for some time, a small quantity of oxamide is likewise formed (Dumas, Liebig):

$$2C^4H^5O,C^4O^6 + NH^3 = C^4H^6O^2 + C^5NH^7O^6.$$

In this reaction, 100 pts. of oxalic ether yield 31·356 pts. of absolute alcohol and 78·672 pts. (76 to 77 pts. according to Dumas) of oxamethane. (Dumas & Boullay.) When the ammoniacal gas and the oxalic ether are both perfectly dry, the greater part of the latter remains undecomposed, even when heat is applied; a large quantity of oxamethane is then formed, with but little oxamide. Absolute alcohol saturated with dry ammoniacal gas does not form any oxamide with oxalic acid, but a clear liquid, which when evaporated leaves a large quantity of oxamethane. (Liebig; *Pogg.* 31, 359.)

7. *Potassium* and *Sodium* heated with oxalic ether decompose it into carbonic oxide, carbonic ether, and other products. — *Sodium* does not act in the cold; when heated to the point at which it softens, it emerges from its crust of oxide, forms yellowish white flocks which gradually become dark red, and at 130° begins to give off gas. By the time that fresh pieces of sodium no longer cause any formation of gas, the quantity evolved amounts to about 586 cubic centimetres for 5·07 grammes of oxalic ether; the gas consists of carbonic oxide mixed with about $\frac{1}{13}$ of its volume of hydrogen or carbonic acid. There remains a dark-red mass, syrupy while warm, but of the consistence of an extract when cold, and having a peculiar odour. This mass dissolves readily in water, carbonic ether then separating and rising to the surface of the liquid. It likewise dissolves completely in absolute alcohol; and this solution evaporated warm over oil of vitriol in vacuo, leaves a vitreous mass, which yields a brown-red powder, quickly becoming moist and gummy. (Ettling, *Ann. Pharm.* 19, 18; also *Pogg.* 39, 157). — Potassium also forms carbonic oxide and carbonic ether, the residue containing oxalate of potash. (Cahours, *N. Ann. Chim. Phys.* 9, 201; also *Ann. Pharm.* 47, 292; also *J. pr. Chem.* 30, 241). The dark colour appears as soon as the sodium begins to act; if the action is strong, heat is produced, and oxalic and carbonic ethers are evolved together with the carbonic oxide; hence the production of the carbonic ether does not depend on the addition of water. The carbonic ether, which amounts to a large quantity, may likewise be distilled off from the mass as soon as formed. The substance then remaining forms with water a black-brown alkaline solution, which yields a large quantity of alcohol by distillation. Sulphuric acid added to the residual liquid throws down black flocks of *Nigric acid*, and the filtrate when distilled yields formic acid, an additional quantity of nigric acid remaining in the retort, while oxalic acid remains in solution. (Löwig & Weidmann).

This *nigric* acid is washed with alcohol and ether as long as the wash-liquids exhibit a brownish colour, then dissolved in alcohol, filtered to separate a trace of undissolved black matter, and evaporated. It may also be obtained by dissolving in water the mass which remains after the distillation of the carbonic ether; precipitating with acetate of lead; washing the brown precipitate; suspending it in water; decomposing with sulphuretted hydrogen; filtering from the sulphide of lead; evaporating the filtrate, which has at first a yellow colour, on the water-bath, in shallow open basins; pouring water on the residue; evaporating again; and treating the nigric acid, now again rendered insoluble, with water, to free it from oxalic acid. When the acid thus obtained is treated with ether, it partly remains undissolved in the form of a black mass; another portion dissolves in the ether, forming a brown solution; but this portion when heated with water is likewise converted into the black acid, which does not dissolve in ether. There are therefore three states of the acid to be distinguished: 1. As set free by sulphuretted hydrogen, with separation of sulphur, in which state it dissolves in water with a pale yellow colour; 2. As produced by imperfect oxidation in the air, in which state it is insoluble in water, but dissolves with brown colour in ether. 3. As produced by perfect oxidation, in which state it is black, and insoluble both in water and in ether, but dissolves in alcohol. The black acid dissolved in alcohol reddens litmus slightly. With aqueous ammonia, potash, and soda, it forms brown-black solutions, which when evaporated leave black, brittle, amorphous masses. The other salts are almost all

insoluble in water, and have a brown or black colour. The ammoniacal solution freed by evaporation from excess of ammonia, forms with acetate of lead a dark brown precipitate, which when dried at 100°, contains 42·72 p. c. PbO, 31·59 C, 3·03 H, and 22·66 O, and is therefore $PbO,C^{14}H^7O^7$ (Löwig & Weidmann, *Pogg.* 50, 107). In former experiments with oxalic ether and potassium *Pogg.* 50, 107), Löwig thought that he observed the formation of croconate of potash and vinic ether.

Of this decomposition of oxalic ether, and formation of carbonic ether, no satisfactory account has yet been given. It is true that $C^{12}H^{10}O^8$ (oxalic ether)$=C^{10}H^{10}O^6$ (carbonic ether) + 2CO. But as the sodium disappears and is absorbed in the mass, we cannot ascribe the result to a catalytic action of the sodium. Perhaps ethylate of sodium ($C^4H^5NaO^2$) is formed at first, together with carbonic ether and carbonic oxide, and all the other products of decomposition are formed by the action of the ethylate of sodium on the excess of oxalic ether likewise present at the commencement of the action:

$$C^{12}H^{10}O^8 + Na = C^4H^5NaO^2 + C^8H^5O^3 + 3CO.$$

Other explanations have been given by Döbereiner (*J. pr. Chem.* 28, 168, and by Löwig & Weidmann, *Pogg.* 50, 117).

Combinations. — Oxalic ether dissolves sparingly in *Water.*

When *Bichloride of Tin* is gradually added to oxalic ether at a temperature below 0°, till the whole solidifies in a mass, needles united in tufts are obtained, from which the oxalic ether is again separated by water (Lewy, *Compt. rend.* 21, 371; also *J. pr. Chem.* 37, 480).

					Lewy.
12 C	72·0	....	17·76	.....	17·59
10 H	10·0	....	2·46	.....	2·56
8 O	64·0	....	15·78	.....	16·22
2 Sn	118·0	....	29·09	.....	29·25
4 Cl	141·6	....	34·91	.....	34·38
$C^{12}H^{10}O^8,2SnCl^2$	405·6	....	100·00	.....	100·00

Oxalic ether dissolves in *Alcohol,* and is precipitated from the solution by water.

¶ Vinomethylic Oxalate.

$C^{10}H^6O^8=C^2H^3O,C^4H^5O,C^4O^6=C^4(Me,Ae,)O^8$.

Chancel. *Laur. & Gerh. C. R.* 1850, 373, 403; *Jahresber.* 1850, 469.

Oxalvinométhylide. — Formed by the action of sulphovinate of potash or oxalomethylate of potash, or of the sulphomethylate on the oxalovinate:

$$\left.\begin{matrix}C^2H^3\\K\end{matrix}\right\}2SO^4 + C^4\left\{\begin{matrix}C^4H^5\\K\end{matrix}\right\}O^8 = C^4\left\{\begin{matrix}C^2H^3\\C^4H^5\end{matrix}\right\}O^8 + \left.\begin{matrix}K\\K\end{matrix}\right\}2SO^4.$$

or:

$$C^2H^3O,KO,2SO^3 + C^4H^5O,KO,C^4O^6 = C^2H^3O,C^4H^5O,C^4O^6 + 2(KO,SO^3).$$

Preparation. — 1 pt. of oxalovinate of potash completely dried, first at 100°, afterwards in vacuo, is intimately mixed with 1 pt. of perfectly

anhydrous sulphomethylate of potassium (and with pumice-stone to facilitate the distillation), and the mixture heated in a retort placed in a sand-bath. On the application of a sufficient heat, the vinomethylic oxalate passes over in the form of a yellow liquid, having a pungent alliaceous odour arising from the presence of a sulphur-compound; from this however it may be freed by several distillations over common salt. It is further purified by shaking it up with cold water, placing it for 24 hours in contact with chloride of calcium, and finally distilling it over oxide of lead.

Properties. — Transparent, colourless liquid, having a faint aromatic odour. Sp. gr. 1·27 at 12°. Distils without alteration, and boils between 160° and 170°. Vapour-density 4·677.

			Chancel.				Chancel.
10 C	60	45·45	45·1	C^2H^3O	23	17·42	
8 H	8	6·06	6·1	C^4H^5O	37	28·03	
8 O	64	48·49	48·8	C^4O^6	72	54·55	54·40
$C^{10}H^8O^8$	132	100·00	100·0		132	100·00	

	Vol.	Density.
C-vapour	10	4.1600
H-gas	8	0·5044
O-gas	4	4·4372
Vapour of $C^{10}H^8O^8$	2	9·1016
	1	4·5508

Vinomethylic oxalate is inflammable, and burns with a bright flame, blue at the edges. It does not dissolve in water without decomposition; cold water and damp air decompose it slowly; boiling water dissolves it completely, decomposing it however into wood-spirit, alcohol, and oxalic acid. In solution of potash, it disappears immediately, even in the cold. Ammonia decomposes it rapidly, forming a precipitate of oxamide (Chancel). ¶

Oxalovinic Acid. $C^4H^6O^2,C^4O^6=HO,C^2O^3+C^4H^5O,C^2O^3$.

Mitscherlich (1834). *Pogg.* 33, 332. — *Lehrb.* Aufl. 4, 1, 208.

Weinoxalsäure, Ætherkleesäure, Acide oxalovinique.

A solution of oxalic ether in absolute alcohol is mixed with a quantity of hydrate of potash dissolved in absolute alcohol, just sufficient to saturate the oxalic acid; the precipitated crystalline scales of oxalovinate of potash are washed on a filter with absolute alcohol, and dissolved in hydrated alcohol, which leaves undissolved the admixed oxalate of potash; the potash separated from the filtrate by an equivalent quantity of sulphuric acid; the alcoholic solution of oxalovinic acid filtered from the sulphate of potash, diluted with water, and saturated with carbonate of baryta; the filtrate evaporated over the water-bath to a syrup, from which the baryta-salt separates in crystals; and from these when dissolved in water, the oxalovinic acid is separated by sulphuric acid.

The *aqueous acid* cannot be concentrated, either over the water-bath or in vacuo, but ultimately leaves crystallized oxalic acid.

The *Oxalovinates* are resolved by boiling with excess of an aqueous fixed alkali into alcohol and an oxalate of the alkali.

Potash-salt. — Crystalline scales, which do not decompose or suffer any loss of weight at 100°. The salt dissolves readily in water and crystallizes out again with difficulty. Scarcely soluble in absolute alcohol, but dissolves with tolerable facility in hydrated alcohol. 100 pts. of the salt decomposed by boiling with caustic potash, yield a quantity of oxalate of potash containing 47·23 pts. of hypothetical anhydrous oxalic acid.

	Crystallized.			Mitscherlich.
KO	47·2	....	30·22	30·41
8 C	48·0	....	30·73	30·90
5 H	5·0	....	3·20	3·01
7 O	56·0	....	35·85	35·68
$C^4H^5KO^2,C^4O^6$	156·2	....	100·00	100·00

$= C^4(K,C^4H^5)O^8 = KO,C^2O^3 + C^4H^5O,C^2O^3$.

The *Baryta-salt* and the *Potash-salt*, which was obtained like the baryta-salt, crystallize from the aqueous solution, after it has been evaporated over the water-bath to a syrupy consistence.

When the aqueous solution of the potash-salt is boiled with chloride of calcium, oxalate of lime is precipitated. Similarly, a mixture of the aqueous potash-salt with acetate of lead or with sulphate of manganese, zinc, cobalt or copper, yields, when heated or set aside for some time, an oxalate of the heavy metal. In contact with protoxide of copper, the aqueous acid yields alcohol and cupric oxalate (Mitscherlich).

b. Sulphur-nucleus. $C^4H^2S^2$.

Bisulphuretted Vinic Ether. $C^4H^2S^2O = C^4H^2S^2,HO$.

Malaguti (1839). *Ann. Chim. Phys.* 70, 354; also *Ann. Pharm.* 32, 29.

Bisulfovinäther, Schwefeläther, Ether sulfuré.

When sulphuretted hydrogen is passed through bichlorinated vinic ether ($C^4Cl^2H^5O$) contained in a retort, a slight rise of temperature takes place, and a small quantity of an oily substance passes over, which is insoluble in water and sinks to the bottom, together with another body which has an offensive odour and dissolves in the water. Towards the end of the process, the distillation must be accelerated by external heat, but even then the product is not much increased, as the residue soon becomes black and viscid. The distillate, if set aside for a few days, solidifies to a soft mixture of needles and scales, together with an oil. If this oil be pressed out between paper, and the residue repeatedly crystallized from boiling alcohol, a mixture of needles and laminæ is first obtained, and afterwards pure needles of bisulphuretted vinic ether. The laminæ of sulphochlorinated vinic ether, which remain dissolved in the mother-liquid, may be separated by further evaporation and cooling, and purified by repeatedly dissolving them in hot alcohol, and removing the needles which appear first as the liquid begins to cool.

Colourless needles, having a faint odour like that of chloride of sulphur, fusing between 120° and 123°, and solidifying on cooling in a hard brittle crystalline mass. (Malaguti.)

				Malaguti.
4 C	24	35·82		35·71
3 H	3	4·48		4·52
2 S	32	47·76		47·01
O	8	11·94		12·76
$C^4H^3S^2O$	67	100·00		100·00

The needles are decomposed by alcoholic potash, yielding sulphide of potassium and acetate of potash:

$$C^4H^3S^2O + 3KO = C^4H^3KO^4 + 2KS.$$

They dissolve in ether and alcohol, but not in water (Malaguti).

c. Iodine-nuclei.

a. Iodine-nucleus. C^4IH^3.

Iodide of Acetyl. C^4IH^3.

Regnault (1835). *Ann. Chim. Phys.* 59, 370; also *Ann. Pharm.* 15, 69.

Emil Kopp. *Compt. rend.* 18, 87; also *J. pr. Chem.* 33, 185.

Sogenanntes Iodacetyl, Iodaldehyden, Iodure d'Acetyle, Iodure d'Aldehydène (the hypothetical radical C^4H^3 being called *Acetyl* or *Aldehydene*); *Iodéthase* (Laurent); [*Vinasch*].

Iodide of ethylene ($C^4H^4I^2$) immersed in strong alcoholic potash, immediately gives off vapour of acetyl. It is ultimately heated to 50° or 60°, to expel the vapour completely, and the vapour passed, first through a small quantity of water, then through a long chloride of calcium tube into a receiver cooled with ice and salt, in which it condenses, whilst olefiant gas, produced at the same time, passes further (Regnault):

$$C^4H^4I^2 + KO = C^4IH^3 + KI + HO.$$

Part of the $C^4H^4I^2$ is, however, resolved into C^4H^4 and 2I. — E. Kopp simply distils the iodide of ethylene with alcoholic potash, passes the alcoholic distillate into a well cooled receiver, and precipitates the oil by water.

Colourless oily liquid (Regnault). Sp. gr. 1·98. Boils at 56° (E. Kopp). Vapour-density about 4·78. Smells like garlic (Regnault); like onions (Kopp).

It is decomposed by fuming nitric acid, with evolution of nitrous fumes and separation of iodine, but not by cold pure nitric acid, or by sulphuric or hydrochloric acid (E. Kopp).

Insoluble in water, but dissolves very easily in alcohol and ether.

		E. Kopp.		Vol.	Density
4 C	24	15·69	15·20	C-vapour	4	1·6640
3 H	3	1·96	2·00	H-gas	3	0·2079
I	126	82·35		I-vapour	1	8·7356
C^4IH^3	153	100·00		Vapour of C^4IH^3	2	10·6075
					1	5·3037

β. Iodine Nucleus. C^4I^3H.

Iodal. C^4I^3H,O^2.

To this head belong probably the two following liquids:

a. A solution of 1 pt. iodine in 4 pts. absolute alcohol, is introduced into a bottle provided with a loosely fitting glass stopper, and strong nitric acid added in about equal quantity. If the brown mixture does not become decolorized in 2 to 8 days, more nitric acid must be added. Gas is then continually evolved, consisting chiefly of nitrous oxide, and an oil is formed, which must be removed with the pipette. As it still retains alcohol, nitric acid, and nitrous ether, it must be distilled over carbonate of lime and chloride of calcium. It begins to boil at 25°; the boiling point rising, however, to 115°, at which temperature the residue decomposes, and the distillate becomes red from separation of iodine. The first portions of the distillate which pass over contain large quantities of nitrous ether; the last portion contains only traces, which may be removed by leaving the liquid for several days in contact with 30 times its bulk of water.

The oil thus obtained smells like chlorine. When kept under water for some days, it forms needles at the surface of contact. It gives off iodine with oil of vitriol, and is converted by potash into iodoform. — It dissolves sulphur, bromine, and chlorine, and dissolves in alcohol and wood-spirit (Aimé, *Ann. Chim. Phys.* 64, 217; also *Ann. Pharm.* 23, 258; also *J. pr. Chem.* 12, 188).

b. When a saturated solution of iodine in alcohol is poured into nitric acid heated in a capacious flask, a violent action ensues; nitric oxide, acetic acid, and nitrous ether are given off; and the iodine-solution becomes decolorized. If the application of heat be continued, fresh iodine added till the action ceases and the colour disappears, and the liquid left to cool, the compound sinks to the bottom in the form of a yellowish oil. — The supernatant acid liquid still deposits a small portion of oil on being mixed with water, and still more when neutralized by potash; but the oil thus separated is more coloured: the most effectual means of extracting it is to shake up the acid liquid with vinic ether.

The oil is clear, of pale yellow colour, and sp. gr. 1·34; has a strong pungent odour, very different from that of iodic ether. It reddens litmus, inasmuch as, from the great facility with which it decomposes, it cannot be freed from adhering acid, either by distillation or by the action of alkalis. Boils at 110°; but decomposes and turns brown at the same time. When exposed to the air, it evaporates very slowly, becoming thick and decolorized; on the hand it evaporates more quickly, leaving a stain of iodine. When heated in a retort, it slowly yields at 71° a colourless distillate, having an ethereal odour, and leaves a dark thick residue, which at 193° likewise volatilizes, giving off iodine-vapours, and leaving a shining carbonaceous residue. — The oil exposed to sunshine in closed vessels, assumes a darker colour, and yields a crystalline deposit of iodine.

Chlorine gas reddens the oil, with formation of hydrochloric acid gas, but without completely decomposing it. — Cold nitric acid has no

action upon the oil. Oil of vitriol turns it brown, and at higher temperatures blackens it, with evolution of iodine and sublimation of yellowish prisms, probably consisting of $C^4H^4I^2$. — Hydrochloric acid slowly colours the oil brown, itself at the same time acquiring a yellow colour. Strong potash-solution decolorizes it, with rise of temperature and evolution of gas, and assumes a red colour; but on agitation with water, the oil becomes somewhat yellowish, and acquires the power of reddening litmus; if the potash-ley is in sufficient quantity, the oil appears to resolve itself into a colourless oily hydrocarbon and iodide of potassium; no iodate of potash is formed. Potassium decomposes the oil, with evolution of heat, leaving a residue of charcoal and iodide of potassium. Phosphorus produces iodide of phosphorus, with great evolution of heat; the same decomposition takes place even under water, which then takes up hydriodic acid. — The oil dissolves abundantly in ether and in alcohol, and is separated from its alcoholic solution by water (Johnston, *Phil. Mag. J.* 2, 415; also *Schw.* 68, 213; also *Ann. Pharm.* 9, 206). — Johnston regards this liquid as *Iodic Ether*.

d. Bromine-nuclei.

a. Bromine-nucleus. C^4BrH^3.

Bromide of Acetyl. C^4BrH^3.

REGNAULT (1835). *Ann. Chim. Phys.* 59, 362; also *Ann. Pharm.* 15, 63.

Sogenanntes Bromacetyl, Bromaldehyden, Bromure d'Acetyle, Bromure d'Aldehydène, Bromêthase (Laurent). [*Vinam*].

An alcoholic solution of bromide of ethylene ($C^4H^4Br^2$) mixed with aqueous potash, spontaneously evolves the vapour of bromide of acetyl, which, on the subsequent application of heat, is given off completely between 30° and 40°. It is passed through a small quantity of water, then through a long chloride of calcium tube, and then into a receiver surrounded with a mixture of ice and salt, in which it condenses quite free from bromide of ethylene:

$$C^4H^4Br^2 + KO = C^4BrH^3 + KBr + HO.$$

Colourless, very thin liquid, which has a sp. gr. of about 1·52, boils even at ordinary temperatures, and forms a vapour of sp. gr. 3·691. Its odour is ethereal and alliaceous, but not unpleasant (Regnault).

			Regnault.			Vol.	Density.
4 C	24	22·43		22·48	C-vapour	4	1·6640
3 H	3	2·80		2·92	H-gas	3	0·2079
Br	80	74·77		74·60	O-gas	1	5·5465
C^4BrH^3	107	100·00		100·00	Vapour of C^4BrH^3	2	7·4184
						1	3·7092

Chlorine converts the liquid into an oil resembling Dutch liquid. If the liquid be enclosed together with bromine in a sealed glass tube, exposed for some days to sunshine, and the point of the bulb then broken

off, a large quantity of acid vapours escape, probably consisting of hydrobromic acid. If the remaining liquid be washed with water containing potash, a liquid is deposited heavier than oil of vitriol, boiling above 100°, and exactly resembling bromide of ethylene; but containing only 9·38 p.c. C and 1·30 H, and consequently too much bromine, perhaps because it contains a bromide of carbon in solution (Regnault). This liquid might be $C^4H^3Br^5$, or as hydrobromic acid is evolved, perhaps C^4HBr^3 (Laurent, *Ann. Chim. Phys.* 60, 327; also *Ann. Pharm.* 18, 165). — Potassium slowly decomposes bromide of acetyl at ordinary temperatures, becoming covered with a crust of bromide of potassium; but when heated, it becomes red-hot and separates charcoal. The vapour also deposits charcoal on strongly or gently heated iron. If the iron is red-hot, a gas is obtained, which smells like naphthalin, and contains in 100 volumes, 110 vol. hydrogen and 90 vol. carbon-vapour; if the iron be less heated, 100 vol. of the gas contain 129 vol. hydrogen and 152 vol. carbon-vapour; and if the iron be still colder, 151 vol. hydrogen and 160 vol. carbon-vapour. (Regnault).

β. Bromine-nucleus. C^4Br^3H.

Bromal. C^4Br^3H,O^2.

Löwig (1832). *Ann. Pharm.* 3, 288. — *Pogg.* 36, 551. — *Org. Verb.* 2, 92.

Formylbromid mit Kohlenacibromid (Berzelius); *Oxyde de Bromēthise* (Laurent). [*Nevinim.*]

Preparation. 1. To 1 pt. of ether or absolute alcohol contained in a cooled distillatory apparatus, 3 or 4 pts. of bromine are gradually added; the mixture set aside for 12 days; and three-fourths of it, consisting of hydrobromic acid, bromide of ethyl, and heavy hydrobromic ether, distilled off; a residue is then left, consisting of bromal mixed with small quantities of heavy hydrobromic ether and hydrobromic acid. This residue mixed with water, and exposed to the air in a shallow basin, for an interval of 12 to 24 hours, yields large crystals of hydrate of bromal. On gently heating these crystals with six times their weight of oil of vitriol, the dehydrated bromal sinks to the bottom as a transparent colourless oil, which is separated mechanically from the greater part of the oil of vitriol, and finally distilled, first over slaked, and then over quick lime. Or the crystallized hydrate may be distilled with oil of vitriol.

2. Three parts of bromine are gradually added to 1 pt. of absolute alcohol contained in a bottle; about $\frac{5}{6}$ distilled off at a gradually increasing heat; the residue, consisting of bromal, heavy hydrobromic ether, hydrobromic acid and formic acid, agitated with a large quantity of ether; the upper ethereal stratum, which contains the bromal and heavy hydrobromic ether in solution (if too little ether be used, it falls to the bottom), separated from the lower liquid containing the two acids; the ether distilled from the upper layer at the gentlest possible heat; the residue exposed to the air in a shallow dish till yellowish crystals of hydrate of bromal form; these crystals pressed between paper to free them from the heavy hydrobromic ether, a portion of which, neverthe-

less, remains adhering to them; and the crystals distilled, as above, with oil of vitriol (Löwig).

According to Aimé, bromal may be prepared like iodal, from alcohol, nitric acid, and bromine.

Properties. Transparent, colourless oil, of sp. gr. 3·34; somewhat greasy to the touch; makes grease-spots on paper, which, however, disappear after a while. Boils above 100°, and may be distilled without decomposition. Has a peculiar pungent odour, and excites a copious flow of tears; its taste is extremely sharp and burning, and very persistent.

				Löwig.
4 C	24	8·54		8·64
H	1	0·36		0·38
3 Br	240	85·41		84·65
2 O	16	5·69		6·33
$C^4Br^3HO^2$	281	100·00		100·00

Decompositions. 1. Bromal passed over red-hot iron yields bromide of iron, charcoal, and carbonic oxide [and hydrogen]. — 2. Heated lime or baryta becomes incandescent in bromal vapour, forming carbonic oxide gas [and water?] and a bromide of the metal mixed with charcoal. These metals do not act when only slightly heated. — 3. Aqueous fixed alkalis decomposed bromine at a gentle heat, yielding formiate of potash and bromoform:

$$C^4Br^4HO^2 + HO,KO = C^2HKO^4 + C^2Br^3H.$$

Chlorine, nitric acid, and oil of vitriol exert no decomposing action; if bromal fumes on the addition of oil of vitriol, it still contains heavy hydrobromic ether.

Combinations. With *Water.* *a. Hydrate of Bromal.* — Bromal exposed to the air is soon completely converted into snow-white crystals of the hydrate. A solution of bromal in a small quantity of water yields, after long keeping, large crystals of the hydrate having the form of sulphate of copper. The crystals fuse even at the heat of the hand; they have the smell and taste of bromal. Oil of vitriol converts them immediately into anhydrous bromal. They dissolve readily in water, and crystallize out again on evaporation.

	Large Crystals.			Löwig.
4 C	24	7·57		7·75
5 H	5	1·58		1·57
3 Br	240	75·71		15·32
6 O	48	15·14		75·36
$C^4Br^3HO^2 + 4Aq$	317	100·00		100·00

b. Aqueous Bromal. The solution has the taste and smell of bromal, does not redden litmus, or precipitate nitrate of silver.

Bromal dissolves *Phosphorus* and *Sulphur.*

It mixes readily with *Bromine.*

Mixes very readily with *Alcohol* and with *Ether* (Löwig).

Conjugated Bromine-compound.

Bromoxaform. $C^6HBr^5O^4$.

CAHOURS. *N. Ann. Chim. Phys.* 19, 488; also *J. pr. Chem.* 41, 62; abstr. *Compt. rend.* 21, 814.

Bromoxaforme. Discovered by Cahours in 1845.

Formed by the action of bromine on aqueous solutions of the alkaline citrates. (Vid. *Citric acid*):

$$C^{12}H^8O^{14} + 2HO + 14Br = C^6HBr^5O^4 + 6CO^2 + 9HBr.$$

Bromine is added by small portions to a concentrated aqueous solution of citrate of potash, till it no longer causes effervescence from escape of carbonic acid, and the liquid begins to assume a reddish colour; the excess of bromine is then neutralized by cautious addition of caustic potash; the oily mixture of bromoxaform, bromoform, and a small quantity of a peculiar substance, which sinks to the bottom, gently distilled with water; the residual oil left to cool to the crystallizing point under water; and the crystalline mass of crude bromoxaform washed with water and then dissolved in alcohol, from which solution pure bromoxaform crystallizes out on cooling.

Crystallizes on cooling from the hot saturated alcoholic solution in long silky needles; from the dilute solution, by spontaneous evaporation in transparent colourless tables. Melts at 74° or 75°; evaporates for the most part undecomposed when heated, merely giving off a small quantity of bromine vapour; and sublimes in highly lustrous needles.

				Cahours.
6 C	36	7·68		7·78
5 Br	400	85·29		85·75
H	1	0·21		0·32
4 O	32	6·82		6·15
$C^6Br^5HO^4$	469	100·00		100·00

May be regarded as acetone $C^6H^6O^2 + 2O$, in which 5H are replaced by 5Br (Cahours); [or as a compound of C^2Br^3H (bromoform) with $C^4Br^2O^4 = C^4Br^2O^2, O^2$, *i.e.* with an aldide of the nucleus $C^4Br^2O^2$].

Bromoxaform heated with oil of vitriol till it boils, is decomposed, with volatilization of bromine and an oily product. — Strong nitric acid does not decompose it even at a boiling heat, but merely dissolves it. — Its solution in potash is decomposed by boiling into bromoform which volatilizes, and a residue of oxalate of potash and bromide of potassium:

$$C^6Br^5HO^4 + 4KO = C^2HBr^3 + C^4K^2O^8 + 2KBr.$$

It does not dissolve in *Water*, even at a boiling heat; is but slightly soluble in gently heated oil of vitriol; insoluble in cold nitric acid, but dissolves in that acid when hot and tolerably strong (the undissolved portion floating on the top in the form of an oil), and crystallizes in needles as the solution cools.

Dissolves in *Wood-spirit* and in *Ether*, and easily in *Alcohol*, especially when hot (Cahours).

e. Chlorine-nuclei.

a. Chlorine-nucleus. C^4ClH^3.

Chloride of Acetyl. C^4ClH^3.

REGNAULT. *Ann. Chim. Phys.* 58, 308; also *Ann. Pharm.* 14, 28.

Sogenanntes Chloracetyl, Chloraldehyden, Chlorure d'Acetyle, Chlorure d'Aldehydène, Chloréthase (Laurent), [*Vinak*]. — First observed by Liebig; examined by Regnault in 1835.

Chloride of ethylene is mixed in a gas-generating apparatus with alcoholic potash, and after four days, when chloride of potassium has settled down, the liquid is distilled in the water-bath at a gradually increasing heat. From 20° to 25°, the liquid begins to boil and gives off a large quantity of gaseous chloride of acetyl, which is purified by passing it, first into a bulb surrounded with ice, then through two Liebig's bulb-apparatus, the first filled with oil of vitriol, the second with potash (to retain alcohol and hydrochloric acid), then through a chloride of calcium tube, then through a small bulb cooled to −13°, in which traces of chloride of ethylene are deposited, and lastly into a small receiver cooled to −22°, in which the chloride of acetyl condenses to a liquid, mixed, however, with a small quantity of chloride of ethylene (Regnault).

$$C^4H^4Cl^2 + KO = C^4H^3Cl + KCl + HO.$$

Thin liquid, boiling between − 18° and − 15° (Liebig). In the gaseous state it has an ethereal odour (Regnault).

			Regnault.			Vol.		Density.
4 C	24·0	38·46		38·90	C-vapour	4		1·6640
3 H	3·0	4·81		4·77	H-gas	3		0·2079
Cl	35·4	56·73		56·33	Cl-gas	1		2·4543
C^4ClH^3	62·4	100·00		100·00	Vapour of C^4ClH^3	2		4·3262
						1		2·1631

The gas burns with a bright yellow flame, green at the edges. Mixed with oxygen gas over mercury and set on fire, it explodes, 1 vol. of the gas absorbing 2½ vol. oxygen, and forming 2 vol. carbonic acid gas, together with water, hydrochloric acid, and calomel. 2 vol. of the gas contain 4 vol. C-vapour, 3 vol. H-gas, and 1 vol. Cl-gas; 4 vol. C-vapour, with 4 vol. O-gas form 4 vol. carbonic acid gas; 2 vol. H-gas with 1 vol. O-gas form water; and 1 vol. H-gas with 1 vol. Cl-gas forms hydrochloric acid. — Electric sparks passed through the gas for some time produce no decomposition. — Potassium does not act upon the gas in the cold, but when slightly heated in it, becomes incandescent, and separates charcoal, together with a small quantity of naphthalin (Regnault).

In the liquid state, it is dissolved sparingly by water, but in all proportions by alcohol and ether (Liebig).

Chlorine transforms it into the compound $C^4H^3Cl^3$ (Regnault).

Monochlorinated Vinic Ether.

$C^4H^4ClO = C^4ClH^3,HO = C^4OClH^2,H^2$?

FEL. D'ARCET (1837). *Ann. Chim. Phys.* 66, 108; also *Ann. Pharm.* 28, 82; also *J. pr. Chem.* 13, 439.

Chlorvinäther. Chloréthéral (D'Arcet), *Ether sulfurique hémichloruré* (Malaguti), *Oxychlorure d'Ethène* (Laurent).

When chloride of ethylene (VIII, 376) is prepared from chlorine and unpurified olefiant gas, and distilled over the water-bath to purify it, pure chloride of ethylene passes over first at 85°, and there remains a residue which does not begin to boil till 140°, the boiling point then continually rising till it reaches 180°. The distillate thus obtained yields, after thorough purification [by what means ?] a transparent, colourless, very thin oil, having a sweetish, ethereal odour; its vapour-density is 4·93.

		D'Arcet.		Vol.	Density.
4 C	24·0	33·61	34·45	C-vapour	4	1·6640
4 H	4·0	5·60	5·41	H-gas	4	0·2772
Cl	35·4	49·58	49·34	Cl-gas	1	2·4543
O	8·0	11·21	10·80	O-gas	½	0·5546
C^4H^4ClO	71·4	100·00	100·00	Vapour of C^4H^4ClO	1	4·9501

Its vapour is therefore monatomic, like that of common ether.

Monochlorinated vinic ether burns with a green flame. Chlorine and ammonia exert no action upon it (D'Arcet).

This compound is doubtless produced, quite independently of chloride of ethylene, by the action of chlorine on the ether-vapour still contained in the olefiant gas. (Regnault.) It is probably also formed at the commencement of the action of chlorine upon pure ether. (Malaguti.)

Monochloracetic Acid. $C^4H^3ClO^4$.

FEL. LEBLANC (1844). *N. Ann. Chim. Phys.* 10, 212.

Chloressigsäure, Acide acétique monochloruré, Acide chloréthasique (Laurent). — Not to be confounded with Dumas's chloracetic acid, which is terchloracetic acid.

Obtained by passing chlorine gas through glacial acetic acid in the shade, as long as any action takes place (it is very slow even at 100°), and then passing dry carbonic acid gas through it at 100°, to expel free chlorine.

Colourless liquid, having the odour of glacial acetic acid, but somewhat less mobile.

The acid decomposes the alkaline carbonates with effervescence, and yields a deliquescent salt with potash.

It does not precipitate nitrate of silver. Diluted with water, saturated at a gentle heat with moist oxide of silver, and filtered, it yields,

on evaporation in vacuo, first a few crystals of ordinary acetate of silver, which must be removed, and then small white shining scales of the chloracetate, which are somewhat more soluble in water than the acetate; change very rapidly when exposed to light, and leave chloride of silver when burnt (Leblanc).

				Leblanc.
4 C	24·0	11·92		11·54
2 H	2·0	0·99		1·02
Ag	108·0	53·62		52·70
Cl	35·4	17·58		
4 O	32·0	15·89		
$C^4ClH^2AgO^4$	201·4	100·00		

Bichlorinated Hydrochloric Ether.

$C^4H^3Cl^3 = C^4ClH^3,Cl^2 = C^4Cl^3H,H^2$?

Regnault (1839). *Ann. Chim. Phys.* 71, 355; also *Ann. Pharm.* 33, 317; also *J. pr. Chem.* 19, 201.

Trichlorvinafer, Acetylchlorid, doppeltchlorhaltiger Chlorwasserstoffäther, Ether hydrochlorique bichloruré.

Monochlorinated hydrochloric ether, $C^4H^4Cl^2$ (VIII, 375), exposed to daylight, rapidly absorbs chlorine gas, assuming a yellow colour, but not decomposing; but if exposed to sunshine, it loses its colour in a few minutes; becomes heated, often enough to cause projection of the liquid; and gives off hydrochloric acid gas (Regnault):

$$C^4H^4Cl^2 + 2Cl = C^4H^3Cl^3 + HCl.$$

700 grammes of monochlorinated hydrochloric ether, covered with a thin layer of water, are introduced into a two-mouthed bottle, one aperture of which is connected by a bent tube with a cooled receiver, while the other serves to convey the chlorine to the bottom of the vessel. The liquid is first saturated with chlorine in a rather dark place, and then transferred to a lighter place, or to direct sunshine, to induce the reaction. After the action of the chlorine has been thus continued for two days, during which time a small quantity of liquid distils over in consequence of the heat evolved (this liquid is rich in chlorine, and may serve for the preparation of sesquichloride of carbon), the liquid in the bottle is distilled over, the receiver being changed after a while,—because the first portion still contains a large quantity of monochlorinated hydrochloric ether, and must therefore be, again subjected for some time to the action of chlorine, after which it may be added to the latter half of the distillate and the whole distilled in a retort provided with a thermometer, the first and last fourths of the distillate being set aside and used for the preparation of terchlorinated and quadrichlorinated hydrochloric ether. The half of the distillate which passes over in the middle of the process at a constant boiling point, is pure bichlorinated hydrochloric ether.

Colourless liquid of sp. gr. 1·372 at 16°; boils at 75°. Vapour-density 4·530. Smells like monochlorinated hydrochloric ether.

		Regnault.		Vol.	Density.
4 C	24·0	18·02	18·25	C-vapour 4	1·6640
3 H	3·0	2·25	2·32	H-gas 3	0·2079
3 Cl	106·2	79·73	79·63	Cl-gas 3	7·3629
$C^4H^3Cl^3$	133·2	100·00	100·20	Vapour of $C^4H^3Cl^3$ 2	9·2348
				1	4·6174

This compound is scarcely acted upon by potash even in the state of boiling alcoholic solution, a small quantity of chloride of potassium separating out after several distillations, while bichlorinated hydrochloric ether passes over unaltered. If the residue of the distillation be then evaporated, exhausted with alcohol, filtered to separate chloride of potassium, and the filtrate evaporated to dryness, the residue thus obtained gives with sulphuric acid a distinct odour of acetic acid. [The acetate of potash is perhaps formed as expressed by the following equation: $C^4H^3Cl^3 + 4KO = C^4H^3KO^4 + 3KCl$.] — Bichlorinated hydrochloric ether exposed to the action of chlorine in sunshine, is converted, first into $C^4H^2Cl^4$, then into C^4HCl^5, and finally into C^4Cl^6 (Regnault).

The so-called Perchloride of Acetyl.

$C^4H^3Cl^3 = C^4ClH^3,Cl^2 = C^4Cl^2H^2,HCl$?

Regnault (1838). *Ann. Chim. Phys.* 69, 151; also *J. pr. Chem.* 18, 80.

Perclorure d'Acetyle, Chlorure de Chloréthase (Laurent). [*Kerinak*].

Dry chlorine gas exerts no action upon gaseous chloride of acetyl, C^4ClH^3, in diffused daylight, but in sunshine it forms products whose nature varies according to the proportions in which the two gases are mixed.

Preparation. Gaseous chloride of acetyl is evolved by gradually heating a mixture of chloride of ethylene and alcoholic potash from 20° upwards; passed through a bulb-apparatus filled with water to remove alcohol-vapour; then through a chloride of calcium tube; and lastly through a bulb-apparatus containing a large quantity of pentachloride of antimony, which must be cooled at first, but afterwards allowed to get warm, to prevent the mass from solidifying. The brown mass, swelled up to double the original volume, which remains after saturation, yields by distillation an ethereal liquid, which is freed from antimony by agitation with water containing hydrochloric acid, and twice rectified over quicklime. The portion which goes over between 95° and 115°, contains Dutch liquid; but the boiling point quickly rises to 115°, where it becomes constant, and at that temperature the compound passes over in the pure state. — 2. Chlorine gas is passed to saturation through chloride of ethylene covered with a layer of water and placed in a dark situation; the yellow liquid then brought into the light, where it loses its colour, becomes heated, and gives off hydrochloric acid, which dissolves in the water; chlorine gas continuously passed through it for two days in the light; the watery stratum decanted, and the oil distilled, rejecting the

small quantity of water to remove the alcohol; and rectified over chloride of calcium.

Colourless liquid of sp. gr. 1·250 at 15°; boils between 35° and 40°. Vapour-density = 3·321; has an alliaceous odour, like that of chloride of acetyl, C^4H^3Cl.

					Vol.	Density.
4 C	24·0	24·79	24·86	C-vapour	4	1·6640
2 H	2·0	2·07	2·28	H-gas	2	0·1386
2 Cl	70·8	73·14	76·92	Cl-gas	2	4·9086
$C^4Cl^2H^2$	96·8	100·00	100·06	Vapour of $C^4Cl^2H^2$	2	6·7112
					1	3·3556

The liquid becomes coloured by keeping, even when sealed up in a glass tube, and deposits a white, non-crystalline substance, which contains 25·06 p.c. C and 2·32 H, and is therefore an isomeric modification. — When poured into a bottle filled with chlorine and exposed to light, it takes fire and deposits soot. But if it be poured into chlorine in the shade and then exposed to daylight for 12 hours, it yields crystals of sesquichloride of carbon, C^4Cl^6, and in sunshine is completely converted into that compound (Regnault):

$$C^4Cl^2H^2 + 6Cl = C^4Cl^6 + 2HCl.$$

Bichlorinated Vinic Ether. $C^4H^3Cl^2O = C^4Cl^2H^3O = C^4OCl^2H,H^2$?

Malaguti (1839). *Ann. Chim. Phys.* 70, 338; also *Ann. Pharm.* 32, 15; also *J. pr. Chem.* 18, 27.

Chloräther, Bichlorvinäther, Ether sulfurique chloruré. — Previously observed by Berthollet and by Liebig: compare VIII, 183, 184, where the mode of formation is likewise given.

Preparation. Chlorine gas washed by water and dried over chloride of calcium is passed by daylight into very pure ether, which must at first be cooled somewhat below 0°. As soon as the absorption diminishes, hydrochloric acid gas mixed with vapour of hydrochloric ether is evolved in such quantity, that the liquid would froth over if it were not cooled. The liquid is afterwards gradually heated, the temperature being at last raised to 90°, and chlorine passed through the liquid all the time. In this manner, after the passage of the chlorine has been continued for 40 hours, a heavy, yellow, fuming liquid is obtained, which boils above 100°. It is freed from the more volatile admixtures by distillation at 100°, and then carefully heated somewhat above 100°, but removed from the fire as soon as it shows any tendency to become darker and give off hydrochloric acid, an effect which generally takes place between 135° and 142°. The residual acid, slightly fuming, and pungent-smelling liquid is washed with water continually renewed, till it exhibits a constant composition (whereupon it diminishes in bulk, becomes neutral, more viscid, specifically heavier, and acquires a more pleasant odour), then dried in vacuo over oil of vitriol and lime, and kept in a bottle to preserve it from contact of damp air. — A small quantity of chloral remains mixed with it.

Transparent, colourless oil, of sp. gr. 1·5008. Smells and tastes like fennel. Neutral.

				Malaguti.
4 C	24·0	22·68		22·49
3 H	3·0	2·84		2·84
2 Cl	70·8	66·92		67·50
O	8·0	7·56		7·17
$C^4H^3Cl^2O$	105·8	100·00		100·00

Decompositions. 1. Bichlorinated vinic ether decomposes below its boiling point, turning brown and giving off hydrochloric acid gas. — 2. Oil of vitriol converts it, with evolution of hydrochloric acid, into a black pitchy mass. — 3. Hydrosulphuric acid gas passed through the liquid sometimes exerts a decomposing action, sometimes not, and apparently under the same circumstances; when it acts, a slight rise of temperature and evolution of hydrochloric acid takes place, and a heavy oil insoluble in water passes over (a mixture of bisulphuretted vinic ether, $C^4H^3S^2O$, and chlorosulphovinic ether C^4H^3ClSO, which crystallizes after several days) together with a liquid soluble in water, and having a very offensive odour. The distillate is of small amount, and is increased by heating the residue, but not much, because the residue soon becomes black and viscid:

$$C^4H^3Cl^2O + HS = C^4H^3ClSO + HCl;$$

and

$$C^4H^3Cl^2O + 2HS = C^4H^3S^2O + 2HCl.$$

4. Bichlorinated vinic ether immersed in water gradually disappears, the products of decomposition dissolving in the water. [Probably as hydrochloric and acetic acid: $C^4H^3Cl^2O + 3HO = C^4H^4O^4 + 2HCl$.] — 5. Bichlorinated vinic ether treated with a current of ammoniacal gas, becomes heated to the boiling point, thickens and turns black, and gives off white vapours having a disagreeable empyreumatic odour. If the ether is dissolved in perfectly absolute alcohol, dry ammoniacal gas produces merely a slight colouring without further action; but if water be not completely excluded, sal-ammoniac separates out, and the liquid is afterwards found to contain acetate of ammonia:

$$C^4H^3Cl^2O + 3NH^3 + 3HO = NH^3,C^4H^4O^4 + 2NH^4Cl.$$

6. Aqueous potash does not act immediately, but alcoholic potash quickly decomposes bichlorinated vinic ether, forming a precipitate of chloride of potassium and a solution of acetate of potash:

$$C^4H^3Cl^2O + 3KO = C^4H^3KO^4 + 2KCl.$$

The chloral likewise present gives rise to the formation of a small quantity of chloroform, which falls down as an oil on adding water to the cold mixture of bichlorinated vinic ether with alcoholic potash; this oil disappears on boiling, either before or after the addition of water, from formation of formic acid. — 7. Potassium does not act in the cold on bichlorinated vinic ether contained in a receiver standing over mercury; but on the application of heat, it becomes covered with chloride of potassium, and gives off a gas which burns with a green flame, and contains C, H, and Cl in the proportion of 44 : 5 : 65 (besides oxygen), and is therefore perhaps C^4H^3ClO = *Ether souschloruré*, *i. e.* bichlorinated ether *minus* 1Cl [?] (Malaguti). — 8. Chlorine gas passed for some time

stationary, and finally rising to 140°. The compound which passes over at 135°, is pure and must be collected apart (Regnault):

$$C^4H^3Cl^3 + 2Cl = C^4H^2Cl^4 + 4HCl.$$

Colourless liquid, heavier then water, and having a peculiar aromatic odour (Laurent). Sp. gr. 1·576 at 19°. Boils at 135°. Vapour-density 5·767. Smells like chloride of ethylene (Regnault).

		Laurent.	Regnault.		Vol.	Density.
4 C	24·0	14·32	14·3	14·43	C-vapour	4	1·6640
2 H	2·0	1·19	1·3	1·23	H-gas	2	0·1386
4 Cl	141·6	84·49	84·4	84·32	Cl-gas	4	9·8172
$C^4H^2Cl^4$	167·6	100·00	100·0	99·98	Vapour of $C^4H^2Cl^4$	2	11·6198
						1	5·8099

The compound burns with a green smoky flame (Laurent). When it is gently heated with pieces of hydrate of potash, a violent action takes place, attended with great evolution of heat and formation of chloride of potassium, and an oil is given off, having a strong, peculiar odour, and probably consisting of C^4HCl^3. The same oil is obtained on boiling the compound with alcoholic potash, and then precipitating by water (Laurent). Alcoholic potash decomposes the compound, with evolution of heat, and precipitation of a large quantity of chloride of calcium, and yields when heated an alcoholic distillate from which water precipitates an oil, doubtless C^4HCl^3, but which gives off hydrochloric acid gas, gradually even when left to itself, and immediately when distilled, and therefore cannot be analyzed (Regnault). — By the further passage of chlorine gas, the compound is converted into C^4Cl^6, and with peculiar celerity in sunshine (Regnault).

γ. Chlorine-nucleus C^4Cl^3H.

Chloral. C^4Cl^3H,O^2.

Liebig. *Ann. Pharm.* 1, 189; also *Pogg.* 24, 252.
Dumas. *Ann. Chim. Phys.* 56, 123; *abstr. Pogg.* 31, 657.
Städeler. *Ann. Pharm.* 61, 101.

Chlorure de Chloréthise [*Nevinik*]. — Discovered in 1832 by Liebig; more minutely examined with respect to its constitution by Dumas.

Formation. 1. By the action of dry chlorine on absolute alcohol (VIII, 212, 213). Dumas' supposition that the chlorine first produces acetic ether, which is then converted into chloral by the further action of the chlorine, is unfounded: for acetic ether is not converted into chloral by chlorine; moreover, perfectly dry chlorine does not form acetic acid with absolute alcohol. It is more probable that the chlorine converts the alcohol into aldehyde by abstraction of 2H; and in this compound, when water is absent, 3 H are replaced by 3 Cl. But in presence of water, the chlorine takes H from that compound, transferring the O to the aldehyde and forming acetic acid, which then with the undecomposed alcohol, yields acetic ether (Liebig, *Pogg.* 40, 299). — 2. By the action of chlorine on starch, grape-sugar, or common sugar (Städeler.)

Preparation. 1. Chlorine gas is passed through absolute alcohol, which is kept cool at first, but afterwards raised to a continually increasing temperature, as long as hydrochloric acid continues to form; the resulting hydrate of chloral freed from water, and a small quantity of alcohol by agitation with oil of vitriol (or by distillation over oil of vitriol: Dumas); and the decanted liquid rectified over lime (Liebig). — The chlorine is evolved continuously from a large retort or flask; passed through a chloride of calcium tube to dry it; and then into a bent tube, the arms of which are short and parallel to each other, but somewhat oblique towards the middle, while that portion of the middle which is directed downwards, and contains the alcohol, is wide, long, and somewhat slanting, so that the chlorine, after arriving at the lowest part, is obliged to pass through the oblique column of alcohol; from this the unabsorbed chlorine, together with hydrochloric acid gas and vapour of hydrochloric ether, passes into two Woulfe's bottles, and thence into the open air, so that the operator is not annoyed by it. At the commencement of the operation, the alcohol is cooled by affusion of cold water, to prevent it from taking fire and depositing soot; but afterwards, when the absorption of the chlorine diminishes, and the liquid assumes a yellow colour, it must be gradually heated, and ultimately nearly to the boiling point. 8 oz. of alcohol require the passage of the chlorine to be continued for 20 days, involving a consumption of 20 pounds of chlorine-mixture. The alcohol becomes continually thicker, acquires a higher boiling point, and is finally converted into a heavy syrup, which, after standing for some days, solidifies completely to a soft white crystalline mass, consisting of hydrate of chloral, together with a small quantity of hydrochloric acid and undecomposed alcohol: *Crude Hydrate of Chloral.* If a sample of the liquid, after being agitated with four times its volume of oil of vitriol and set aside, does not in a few hours form a solid stratum (of insoluble chloral) above the oil of vitriol, the passage of the chlorine must be continued for a still longer time. The solidified crystalline mass is heated till it melts; briskly agitated with 4 to 6 times its bulk of oil of vitriol, which does not heat or blacken it; left at rest till the dehydrated chloral has risen to the top of the oil of vitriol, a result which may be accelerated by gentle heating; and the transparent, colourless film of chloral immediately decanted by means of a pipette. If the oil of vitriol contains rather more than 1 At. water, it is particularly necessary to decant as quickly as possible, before the chloral is thereby converted into insoluble chloral. Lastly, the chloral is distilled over lime which has been slaked and subsequently ignited, to remove hydrochloric acid, care being taken to keep the whole of the lime below the surface of the liquid, as it will otherwise decompose the vapour and become red hot. In this manner, the chloral is obtained tolerably pure; but it still contains traces of water and alcohol, which may be removed by repeated treatment with oil of vitriol, the chloral being each time rectified over lime. All these operations must be performed in well closed vessels (Liebig). — The quantity of salt and manganese required for the whole process, may also be introduced at once into a flask of 15 or 20 litres capacity, and the sulphuric acid gradually poured in through an S-tube. The chlorine is passed through bent tubes, first into an empty Woulfe's bottle, wherein it deposits the greater part of its water; then into a bottle filled with pieces of chloride of calcium; then again into an empty bottle, to prevent injury to the product in case of any of it passing backwards; and, lastly,

to the bottom of the flask containing the alcohol, from which the acid gases are conveyed by a long tube into the chimney. As soon as the alcohol begins to exhibit a yellow colour, it must be gently heated, and the temperature continually raised, a rapid stream of chlorine being kept up all the time, till it no longer acts on the liquid, even at a nearly boiling heat. In this process, 12 hours' work suffices for 200 grms. of alcohol, and 3 days at the utmost for 600 grms. — 250 grms. alcohol require at least 1200 litres of chlorine gas, and give off about 1500 litres of hydrochloric acid gas. — The crude hydrate of chloral thus obtained is mixed with twice its bulk of oil of vitriol, and immediately distilled, a process which goes on readily at a moderate heat, inasmuch as the chloral rises to the surface of the oil of vitriol; the distillation must, however, be interrupted before all the chloral has passed over. The distillate is then boiled, with a thermometer immersed in it, till the boiling point has risen to between 94° and 95°, in order to free it from hydrochloric acid, ether, and perhaps also from alcohol. The residue is then distilled as before over oil of vitriol, and the distillate again boiled. Lastly, it is rectified in a bath of saturated solution of common salt, with not too large a quantity of lime, which has been slaked and then burnt again, care being taken however that the lime is completely covered by the liquid, to prevent the liquid from being set on fire: hydrate of chloral then remains behind, together with the hydrochloric acid, inasmuch as it is less volatile, and the distillate consists of pure chloral (Dumas).

Hydrate of chloral may also be obtained by distilling absolute alcohol, previously saturated with hydrochloric acid gas, with excess of manganese and strong hydrochloric acid; or by distilling 3 pts. of absolute alcohol with 46 pts. of oil of vitriol, 32 pts. common salt, and 24 pts. manganese: this process, however, does not appear to be advantageous (Gm).

2. Starch or sugar is distilled with hydrochloric acid and peroxide of manganese, and the chloral which passes over, purified (Städeler). — 1 pt. of starch (grape-sugar or common sugar) is added to 7 pts. of commercial hydrochloric acid, which must be as free as possible from sulphurous acid; an equal volume of water added; the mixture gently warmed, till the paste (formed when starch is used), has become liquid; the liquid, when cold, introduced, together with 3 pts. of manganese and a small quantity of common salt (to fix the sulphuric acid produced from the sulphurous acid in the commercial hydrochloric acid), into a capacious flask; heated as quickly as possible to the boiling point; and the fire then completely removed. The mass swells up, giving off a large quantity of carbonic acid, and continues to boil for some time by itself. As soon as the ebullition slackens, it must be kept up by fresh application of heat, and the distillate collected, as long as it becomes turbid when mixed with tolerably strong potash-ley (in consequence of separation of chloroform from the chloral). More hydrochloric acid is then repeatedly introduced into the flask by small portions, till the distillate no longer smells of chloral or becomes turbid with potash. The watery distillate is carefully freed from the colourless oil-drops, heavier than water and smelling of chloroform, which are produced at the beginning of the distillation; saturated with common salt, in order to raise its boiling point and retain the water; distilled again; the resulting distillate freed from a sulphur-yellow, very pungent-smelling oil; and distilled several times more with common salt, removing the oily drops, in order to obtain aqueous chloral as concentrated as possible, and as free as possible from the yellow oil, which greatly impedes the purifica-

flakes (Liebig). — When chloral is left for some time in contact with oil of vitriol containing rather more than 1 At. water, it is transformed into the insoluble modification. The mixture of crude hydrate of chloral (p. 202), with oil of vitriol, solidifies in a similar manner when left for some hours, either in a close vessel or exposed to the air (Liebig). — Pure chloral left in contact with six times its volume of oil of vitriol, is likewise converted, in the course of a night, into a white mass of insoluble chloral (Dumas).

Chlorine exerts no decomposing action upon chloral, even at the boiling point of that liquid and in sunshine (Dumas).

2. Fuming nitric acid, if ultimately aided by heat, converts chloral into terchloracetic acid $C^4Cl^3HO^4$; so likewise does a mixture of chlorate of potash and hydrochloric acid (Kolbe, *Ann. Pharm.* 54. 184). According to Dumas, ordinary nitric acid does not act upon chloral, even when heated.

3. Chloral may for the most part be distilled unchanged over oil of vitriol; only towards the end of the distillation is a slight decomposition indicated by the evolution of hydrochloric acid and blackening of the oil of vitriol (Liebig). When hydrate of chloral, but not dry chloral, is heated with oil of vitriol, part of the chloral passes over in the dehydrated state, while the rest is converted, with evolution of hydrochloric, sulphurous, and a small quantity of carbonic acid, into chloralide, (p. 207), (Städeler). Hence to detect the presence of chloral in a liquid, the liquid may be concentrated by several distillations over chloride of calcium; heated for some time with six times its bulk of oil of vitriol to 125°; diluted when cold with a sixfold quantity of water, whereupon a mixture of chloralide and carbonaceous particles separates out; and the mixture washed, pressed between paper, and exhausted with ether, which on evaporation yields crystals of chloralide: these crystals may be further purified by heating with oil of vitriol and recrystallization from ether, after which they may be recognized by their characteristic properties (Städeler).

4. Anhydrous metallic oxides, such as baryta, strontia, lime, cupric oxide, mercuric oxide, or peroxide of manganese, exert no action upon chloral when that liquid is distilled over them. If however the baryta, strontia, or lime be not quite covered by the chloral, or if either of these substances be heated in the chloral vapour only to 100°, it becomes red-hot, and is converted, with evolution of carbonic oxide gas, into a metallic chloride mixed with finely divided charcoal (Liebig). A yellowish oil is at the same time evolved, and the metallic chloride is mixed with a brown substance (Dumas). — 5. Alkalis, either in the form of hydrates or dissolved in water, decompose chloral readily, even at ordinary temperatures, causing evolution of heat, and converting the chloral into chloroform which sinks to the bottom as an oil, formiate of potash, and metallic chloride (Liebig). The first products of the action are formiate of potash and chloroform, and a portion of the latter is further decomposed into formiate of potash and metallic chloride (Dumas):

$$C^4HCl^3O^2 + HO,KO = C^2HKO^4 + C^2HCl^3;$$

and

$$C^2HCl^3 + 4KO = C^2HKO^4 + 3KCl.$$

6. The vapour of chloral passed over red-hot iron yields carbonic oxide and chloride of iron covered with charcoal (Liebig). — 7. Potassium in contact with chloral yields hydrogen gas, and produces a resinous

body from which water extracts potash and chloride of potassium (Löwig, *Pogg.* 43, 624).

Combinations. With *Water.* *a. Hydrate of Chloral.* Chloral shaken up with a small quantity of water combines with it immediately, causing evolution of heat, and solidifies in a few seconds to a white, opaque, crystalline mass. A few drops of chloral spread over a vessel the air of which is not quite dry, soon become covered with numerous stellate crystallisations of the hydrate. A mixture of equal volumes of chloral and water, the formation of which is attended with evolution of heat, yields by evaporation rhombic crystals of the hydrate, which evaporate when exposed for some time to the air. The vapour-density of hydrate of chloral is 2 76 (Dumas).

		Dumas.		Vol.	Density.
4 C	24·0	14·53	14·51	C-vapour 4	1·6640
3 H	3·0	1·82	1·79	H-gas 3	0·2079
3 Cl	106·2	64·28	63·12	Cl-gas 3	7·3629
4 O	32·0	19·37	20·58	O-gas 2	2·2186
$C^4HCl^3O^2 + 2Aq$	165·2	100·00	100·00	Vapour 4	11·4534
				1	2·8633

b. Aqueous Chloral. Chloral dissolves readily and abundantly in water. The hydrate mixed with a small quantity of water is immediately converted into oily drops which dissolve when heated. The solution smells of chloral and has no particular taste. As it does not reduce mercuric oxide at a boiling heat, it must contain the chloral in the undecomposed state (Liebig).

Chloral, especially with the aid of heat, readily dissolves *phosphorus, sulphur, iodine* (the latter with purple colour) and *bromine* (Liebig). — Chloral absorbs a small quantity of *chlorine gas,* acquiring thereby a yellow colour (Dumas).

Insoluble Chloral.

For the literature vid. Chloral, p. 200.

Unlosliches Chloral, Chloral insoluble. — Discovered by Liebig.

Formation. (p. 201). According to Städeler, it is only the insoluble product formed from soluble chloral, either alone or with the aid of water, that constitutes the true insoluble chloral, the product obtained by the action of sulphuric acid upon chloral, being a mixture of chloralide and insoluble chloral. But the formation of chloralide seems to require the aid of heat; Liebig and Dumas performed the process at ordinary temperatures. The infusibility of the products which they obtained, and the insolubility of the same products in alcohol and ether, are unfavourable to Städeler's supposition.

Preparation. 1. Pure chloral prepared by Dumas' method is left to itself in a closed vessel till it is converted into a white amorphous porcelain-like mass insoluble in water (Regnault, *Ann. Chim. Phys.* 71, 409; also *Ann. Pharm.* 34, 36; *J. pr. Chem.* 19, 280). The small quantity of residual liquid behaves like insoluble chloral. — 2. Chloral is

mixed with a quantity of water less than sufficient to form the hydrate (Liebig). — *a*. The solidified mass is completely freed from soluble chloral by repeatedly pouring water on and off it, till it no longer exhibits any acid reaction, after which it is dried over chloride of calcium (Städeler). — *b*. The mass *a* is further heated for a short time to a temperature between 100° and 120°, till the hydrate of chloral is volatilized (Städeler). — 3. Crude hydrate of chloral (p. 202) mixed with four times its weight of oil of vitriol, and set aside for some hours, either in an open or in a closed vessel, solidifies to a porcelain-like mass which is freed from unaltered chloral and from sulphuric acid by washing with hot water (Liebig). For whatever time the washing may be continued, the liquid which runs off still exhibits an acid reaction, perhaps in consequence of gradual decomposition (Liebig). — 4. Chloral left over-night in contact with a six-fold quantity of oil of vitriol, solidifies to a white opaque mass, which, after a few days, is to be diffused in water, triturated, thrown upon a filter, washed with boiling water, and dried (Dumas).

Properties. Insoluble chloral (3) is a snow-white powder which volatilizes slowly in the air, emitting a faint, peculiar, ethereal odour (Liebig); (4) volatilizes slowly in vacuo (Dumas).

			Regnault.	Städeler.		Liebig.	Dumas.
			(1)	(2, *a*)	(2, *b*)	(3)	(4)
4 C	24·0	16·30	16·27	16·55	16·33	17·64	17·76
H	1·0	0·68	0·98	0·98	0·89	1·17	1·14
3 Cl	106·2	72·15	70·90	71·54	71·54	67·10	67·74
2 O	16·0	10·87	11·85	10·93	11·24	14·09	13·36
$C^4HCl^3O^2$	147·2	100·00	100·00	100·00	100·00	100·00	100·00

The compound is therefore isomeric with soluble chloral. The analyses made by Liebig and Dumas lead to the suspicion that their products were contaminated with chloralide; but the observed insolubility of the same in alcohol and ether points to a contrary conclusion.

Decompositions. 1. When insoluble chloral (3) is distilled, a viscid product is obtained resembling soluble chloral, but solidifying again after a while (Liebig). Insoluble chloral (4) heated to 150° and even to 200°, does not melt, but yields a very volatile distillate crystallizing like hydrate of chloral, and leaves a trace of charcoal (Dumas). Insoluble chloral (1) heated in the oil-bath to between 200° and 250°, distils over in the form of perfectly pure soluble chloral (Regnault). Insoluble chloral (3), when properly dried, may be converted without loss into soluble chloral by distillation at 180° (Kolbe, *Ann. Pharm.* 54, 133):— 2. Insoluble chloral (3) is decomposed by nitric acid, slowly and with effervescence (Liebig); like soluble chloral, it is converted by fuming nitric acid into chloracetic acid (Kolbe). On the other hand, it is not attacked by a mixture of hydrochloric acid and chlorate of potash (Kolbe). — 3. When (3) is distilled with oil of vitriol, the greater part of it passes over as transparent and colourless soluble chloral, which however, after some hours or days, again solidifies to a white mass; but hydrochloric acid likewise passes over, and the residue turns black (Liebig). — 4. The product (3) dissolves in aqueous alkalis, and is completely decomposed, with production of an alkaline formiate and chloroform; the quantity of the latter is smaller in proportion as the alkali is more concentrated. When (3) is fused with hydrate of potash, very little or no chloroform is obtained, but, in the latter case, a substance which dissolves with brownish

colour in the alkali (Liebig). The product (4) behaves with alkalis like soluble chloral (Dumas).

Insoluble chloral (3 and 4) is insoluble in cold water and dissolves very sparingly in boiling water (Liebig, Dumas). — It does not dissolve in alcohol or ether, even at a boiling heat (Liebig, Dumas).

Appendix to Chloral.

Chloralide.

STÄDELER. *Ann. Pharm.* 61, 104.

Formation. Hydrate of chloral dissolves with tolerable facility in oil of vitriol; the solution when slowly and gently heated, gives off sulphurous acid and a small quantity of carbonic acid, together with undecomposed hydrochloric acid, and without blackening, becomes covered with white crystalline chloralide. As the evolution of hydrochloric acid gradually diminishes, the chloralide separates out in soft shining needles, uncontaminated with any trace of an oily product. — Städeler, who assigns to chloralide the formula $C^{10}H^2Cl^6O^6$, and regards the formation of the oil as unessential, gives the equation:

$$4C^4HCl^3O^2 + 4HO = C^{10}H^2Cl^6O^6 + 6HCl + 6CO.$$

It is true, he did not actually observe the presence of carbonic oxide; but he suggests that it may have been converted by the sulphuric acid into sulphurous and carbonic acid [he however obtained but a small quantity of carbonic acid]. — [If we assume for chloralide the formula $C^8H^2Cl^5O^5$, the equation is:

$$2C^4HCl^3O^2 + HO = C^8H^2Cl^5O^5 + HCl].$$

Water appears to be essential to the formation of chloralide; for anhydrous chloral may be distilled without decomposition over a small quantity of oil of vitriol, without leaving any residue of chloralide (Städeler).

Preparation. 1 vol. hydrate of chloral is heated in a retort with 4 or 5 vol. pure oil of vitriol, gently at first, but afterwards in the oil-bath to 120°—130°, as long as chloral continues to pass over — the mixture being several times briskly shaken during the operation; the chloral reconverted into hydrate by the addition of a small quantity of water and poured back upon the residue when cold; the mixture redistilled between 120° and 130°; the distilled chloral again converted into hydrate, poured back again, &c. &c., till the evolution of gas has nearly ceased, and the chloral no longer distils over, but is converted into chloralide, and floats on the oil of vitriol as a transparent and colourless layer, which solidifies, even above 100°, to a snow-white crystalline mass. The contents of the retort when cold are poured into a funnel loosely stopped with asbestus; the chloralide which remains there exposed for some time to the air, so that the adhering oil of vitriol, being diluted by the moisture of the air, may more easily run off, — after which the chloralide may be washed with water, without fear of heating, till the wash-water no longer reddens litmus. The crystals are then pressed between paper, dissolved in ether, and the solution diluted with half its volume of strong alcohol, and left to crystallize by spontaneous evaporation. The resulting crystals are still contaminated with an oil, to free them from which they are separated from the mother-liquid, redissolved in alcohol, the solution mixed with ether, left to crystallize, &c., till the crystals

appear quite hard and regular, and melt between 112° and 114°. The several mother-liquors run off during these processes yield more crystals, which may be purified in a similar manner by recrystallization.

Properties. Small, transparent, colourless, prismatic crystals, having a vitreous lustre, and united in stellate groups. The crystals are oblique rectangular prisms belonging to the singly oblique prismatic system, and having the obtuse lateral edges truncated. The compound melts to an oil between 112° and 114°, and solidifies again to a crystalline mass between 106° and 105°. Chloraldide still contaminated with the above mentioned oil melts below 100°, and solidifies in a less distinctly crystalline form, often even amorphous. It boils at 200°, and may be distilled over without decomposition. In the cold it smells but slightly; but when heated, it gives off a strong pungent odour like that of chloral. Tasteless by itself, but the alcoholic and ethereal solutions have a sharp, caustic taste.

Calculation, according to Städeler.

10 C	60·0	18·61
2 H	2·0	0·62
6 Cl	212·4	65·88
6 O	48·0	14·89
$C^{10}H^2Cl^6O^6$	322·4	100·00

Calculation, according to Gm.			Städeler. a.		Städeler. b.		c.
8 C	64	17·98	18·74		18·55		20·0
2 H	2	0·75	0·79		0·75		0·9
5 Cl	177	66·29	66·46		65·93		
5 O	40	14·98	14·01		14·77		
$C^8H^2Cl^5O^5$	283	100·00	100·00		100·00		

[The chloralide *a* analysed by Städeler was the purest; *b* had been less completely freed from the oil by a smaller number of crystallizations; and *c* had been crystallized still less frequently. Did *a* likewise still retain some of the oil, and therefore yield somewhat too much carbon?]

Decompositions. Chloralide when set on fire burns with a very bright flame, green at the lower edge. — In a warm aqueous solution of potash, it is resolved into chloroform and formiate of potash:

$$C^{10}H^2Cl^6O^6 + 3HO + 3KO = 2C^2HCl^3 + 3C^2HKO^4.$$

[or:

$$C^8H^2Cl^5O^5 + 2HO + 5KO = C^2HCl^3 + 3C^2HKO^4 + 2KCl;$$

in this case, however, chloride of potassium should be formed, and the decision of this question would likewise show which of the two formulæ, $C^{10}H^2Cl^6O^6$ or $C^8H^2Cl^5O^5$ (neither of which indeed is very probable), should be preferred.] An alcoholic solution of chloralide, treated with alcoholic potash, yields nothing but formiate of potash and chloride of potassium, because the chloroform is at the same time converted into formiate of potash and chloride of potassium. — An alcoholic solution of chloralide does not act upon a solution of nitrate of silver till heated, and even then gives only a faint white cloudiness; when mixed with a small quantity of silver-solution, and then with a drop of ammonia, it yields a precipitate of chloride of silver.

Compounds. Chloralide is insoluble in water, dissolves readily in ether, sparingly in cold, and abundantly in boiling alcohol, from which it crystallizes on cooling, in snow-white, microscopic crystals (Städeler).

Terchloracetic Acid. $C^4HCl^3O^4 = C^4Cl^3H,O^4$.

Dumas. *J. Chim. méd.* 6, 659; also *Ann. Pharm.* 32, 101; also *J. pr. Chem.* 17, 202; abstr. *Pogg.* 20, 166. — *Ann. Chim. Phys.* 73, 75.
Melsens. *N. Ann. Chim. Phys.* 10, 233; also *N. J. Pharm.* 5, 281; also *J. pr. Chem.* 26, 57.
Malaguti. *N. Ann. Chim. Phys.* 16, 10; abstr. *Compt. rend.* 19, 578.
Kolbe. *Ann. Pharm.* 54, 182.

Trichloressigsäure, Chloressigsäure, Chloroxalsäure, Oxalacichlorid (Berzelius), *Chlorkohlenoxalsäure* (Kolbe), *Acide chloracétique, Acide chloroxalique.* — Discovered by Dumas in 1830.

Formation. 1. By the action of dry chlorine gas on glacial acetic acid in sunshine (Dumas):

$$C^4H^4O^4 + 6Cl = C^4HCl^3O^4 + 3HCl.$$

2. In the oxidation of soluble chloral by a mixture of hydrochloric acid and chlorate of potash, and of soluble or insoluble chloral by fuming nitric acid (Kolbe):

$$C^4H^3Cl^3O^2 + 2O = C^4HCl^3O^4.$$

3. By the action of chlorine gas in sunshine on protochloride of carbon covered with a layer of water (Kolbe):

$$C^4Cl^4 + 4HO + 2Cl = C^4HCl^3O^4 + 3HCl.$$

Part of the C^4Cl^4 is at the same time converted into C^4Cl^6. — 4. In the decomposition of chloraldehyde by water (Malaguti):

$$C^4Cl^4O^2 + 2HO = C^4HCl^3O^4 + HCl.$$

5. In the decomposition of perchlorinated formic ether (C^4Cl^5O,C^2ClO^3) by water (Cloez, *N. Ann. Chim. Phys.* 17, 300):

$$C^6Cl^6O^4 + 4HO = C^4HCl^3O^4 + 2CO^2 + 3HCl.$$

Preparation. 1. When glacial acetic acid is introduced into a number of bottles of 6 litres capacity, 5·4 grm. into each, and the bottles filled with dry chlorine gas, closed with their stoppers, and exposed to the sun, they appear on the following day coated with crystals of terchloracetic acid and a small quantity of oxalic acid. In very hot weather, an explosion may take place after a while, but this rarely happens. One of the bottles is then opened, whereupon a mixture of hydrochloric acid gas, with a small quantity of carbonic acid and a suffocating vapour escapes with force; exposed for some hours to the air, till the gaseous mixture is completely expelled; and washed out with 30 or 40 grm. water, which is afterwards used to wash out all the other bottles, so that with 15 or 20 bottles, a concentrated solution of terchloracetic acid is at once obtained, mixed, however, with hydrochloric acid, undecomposed acetic acid, and oxalic acid. When this solution is evaporated in vacuo over oil of vitriol and hydrate of potash, water, hydrochloric acid, and part of the acetic acid escape, and the solution then yields crystals, first of oxalic, and afterwards of terchloracetic acid. The mother-liquor distilled with dry phosphoric acid, whereby the oxalic acid is decomposed, yields

a distillate, first of acetic acid, then, on changing the receiver, of terchloracetic acid, which soon solidifies to a crystalline mass. Lastly, the crystals must be left for some hours in vacuo on several sheets of white blotting paper, so that the admixed acetic acid may soak into the paper (Dumas).

2. Insoluble chloral is treated with fuming nitric acid, and the action, which is at first attended with rise of temperature and abundant evolution of red fumes, is afterwards assisted by the application of a gentle heat, till the flakes of insoluble chloral have completely disappeared; the excess of nitric acid distilled off for the most part; and the remaining portion left to evaporate in vacuo over oil of vitriol and hydrate of potash. Crystallized terchloracetic acid then remains, free from nitric, acetic, and oxalic acid, but generally retaining traces of chloral, which greatly impedes the preparation of pure salts of terchloracetic acid (Kolbe).

3. Protochloride of carbon, C^4Cl^4, is placed in a bottle filled with chlorine gas, covered with a film of water, and exposed to the sun, whereby, besides C^4Cl^6, there is formed an aqueous solution of terchloracetic acid, which may be obtained in the crystalline state by evaporation in vacuo over oil of vitriol and lime (Kolbe).

4. Chloraldehyde is dissolved in water; and the solution containing hydrochloric acid, evaporated in vacuo over oil of vitriol and hydrate of potash, whereby terchloracetic acid is obtained in beautiful crystals (Malaguti). — For this purpose, dry ether is saturated in sunshine with dry chlorine gas, the products of which action are either sesquichloride of carbon and chloraldehyde,—in which case, the liquid is warmed to drive off the free chlorine, then mixed with water and filtered from the C^4Cl^6,— or else, perchlorinated vinic ether, which is converted by distillation into C^4Cl^6 and chloraldehyde, and the latter decomposed with water as above (Malaguti).

Properties. Colourless rhombohedrons. Melts above 46°, and in cooling begins to solidify at 45°, whereupon, if the mass be shaken, the temperature rises to 46°, which is therefore the melting point. In the fused state, it has a density of 1·617 at 46°, that of water at 15° being 1·000. Boils between 195° and 200° without any decomposition, and sublimes in the form of a silvery crust. Vapour-density = 5·3. It came out too low, because at the high temperature which was necessary, a small quantity of hydrochloric acid was produced. — The acid smells faintly at ordinary temperatures, but when heated till it volatilizes, emitting a pungent and suffocating odour. Has a caustic, sour taste, and makes the tongue white, like peroxide of hydrogen. It destroys the cuticle, causing it to peel off on the following day, and if left for some time on the skin, produces blisters. It reddens litmus strongly, but does not bleach it, even after a considerable time (Dumas).

	Crystallized.		Dumas.		Vol.	Density.
4 C	24·0	14·71	15·50	C-vapour	4	1·6640
H	1·0	0·61	0·75	H-gas	1	0·0693
3 Cl	106·2	65·07	63·75	Cl-gas	3	7·3629
4 O	32·0	19·61	20·00	O-gas	2	2·2186
C^4Cl^3H,O^4	163·2	100·00	100·00	Vapour	2	11·3148
					1	5·6574

The quantity of chlorine obtained was too small, in consequence of the presence of acetic acid (Dumas).

Decompositions. 1. When the acid is heated with oil of vitriol, part of it distils over unchanged, and crystallizes in rhombohedrons; the rest is resolved into hydrochloric acid, carbonic acid, and carbonic oxide (Dumas). [Perhaps in this manner: $C^4HCl^3O^4+2HO=3HCl+2CO+2CO^2$]. — 2. When it is heated with excess of potash-solution, ebullition takes place, continuing after the vessel has been removed from the fire; the first products of the action are chloroform and carbonate of potash; but on further boiling with the alkaline liquid, the chloroform is resolved into formiate of potash and chloride of potassium (Dumas). — First:

$$C^4HCl^3O^4 + 2KO = 2(KO,CO^2) + C^2HCl^3;$$

then:

$$C^2HCl^3 + 4KO = C^2HKO^4 + 3KCl.$$

When the acid is boiled with baryta-water, carbonate of baryta is precipitated and carbonic acid [chloroform] evolved (Dumas). — 3. The acid boiled with excess of ammonia, is resolved into carbonate of ammonia which sublimes, and chloroform which sinks down as an oil (Dumas):

$$C^4HCl^3O^4 + 2NH^3 = 2(NH^3,CO^2) + C^2HCl^3.$$

4. Aqueous terchloracetic acid, or either of its salts dissolved in water, is decomposed by potassium-amalgam (1 pt. potassium to 150 pts. mercury) with evolution of heat, and reconverted into acetate of potash (Melsens):

$$[C^4Cl^3KO^4 + 3HO + 6K = C^4H^3KO^4 + 3KCl + 3KO].$$

If the amalgam is not in excess in proportion to the acid, no hydrogen is evolved. The decomposition is soon completed. If the resulting potash be then saturated with carbonic acid gas, the solution evaporated to dryness, and the residue treated with alcohol, the alcohol extracts acetate of potash, leaving a mixture of chloride of potassium with carbonate of potash. Antimonide of potassium, or potassium alone, or zinc with sulphuric acid, does not effect the transformation, but causes an evolution of hydrogen gas (Melsens). — If instead of 6 At. potassium, only 3 At. be used in the form of potassium-amalgam, no acetic acid is produced, but apparently an acid containing a smaller quantity of chlorine than terchloracetic acid. Zinc dissolves in aqueous terchloracetic acid, and forms, besides chloride of zinc, a zinc-salt which appears to contain the otherwise unknown acid $C^4Cl^2H^2O^4$. Terchloracetic acid is also reduced to acetic acid in the galvanic circuit of a two-pair Bunsen's zinc-carbon battery, with electrodes of amalgamated zinc (Kolbe, VII, 297).

Combinations. The acid deliquesces in the air, and dissolves very readily in *water* (Dumas).

Terchloracetate of Ammonia. — The aqueous acid saturated with ammonia, and evaporated at ordinary temperatures, either in vacuo or in the air, yields crystals (Dumas). — The salt is likewise produced when chloracetamide is brought in contact with aqueous ammonia or very dilute nitric acid (Malaguti, Cloez). Crystallizes in beautiful prisms; melts at 80°; boils between 110° and 115°, giving off vapours of chloroform and carbonate of ammonia, the latter appearing in peculiar abundance at 145°; and solidifies at 160° in yellowish, micaceous scales of anhydrous terchloracetate of ammonia, which are tasteless, dissolve readily in water, and give off ammonia when treated with potash, even in the cold. At a higher temperature, these scales fuse, and are resolved into carbonic oxide, phosgene, and sal-ammoniac vapour (Malaguti).

Decomposition of the crystallized salt:

$$C^4NH^5Cl^3O^5 = C^2HCl^3 + NH^4O,2CO^2,HO + 2HO.$$

Decomposition of the residual anhydrous salt:

$$C^4NH^4Cl^3O^4 = 2CO + 2ClO + NH^4Cl.$$

	Dehydrated in vacuo.			Dumas.
4 C	24·0	13·32		13·5
N	14·0	7·77		
4 H	4·0	2·22		2·2
3 Cl	106·2	58·93		
4 O	32·0	17·76		
$C^4(Cl^3,NH^4)O^4$	180·2	100·00		

	Air-dried crystals.			Dumas.
4 C	24·0	11·10		10·4
N	14·0	6·48		6·5
8 H	8·0	3·70		4·2
3 Cl	106·2	49·12		
8 O	64·0	29·60		
$C^4(Cl^3,NH^4)O^4 + 4Aq$	216·2	100·00		

Dumas supposes the salt to contain 5 At. water of crystallization; Malaguti 4 At.

Terchloracetate of Potash. — The aqueous acid neutralized with carbonate of potash yields by spotaneous evaporation, silky needles, which decompose with a kind of detonation when gently heated, and absorb only a small quantity of water when exposed to damp air (Dumas).

	Crystallized.			Dumas.	Kolbe.
KO	47·2	22·43		23·00	22·34
4 C	24·0	11·41		11·06	
H	1·0	0·48		0·70	
3 Cl	106·2	50·47			
4 O	32·0	15·21			
$C^4Cl^3KO^4 + Aq$	210·4	100·00			

The *Baryta* and *Lime salts* are neutral and dissolve very readily in water (Dumas).

Terchloracetate of Silver. — Recently precipitated oxide of silver immersed in the aqueous acid is converted into grey laminæ which dissolve in a larger quantity of water, and crystallize therefrom by evaporation in vacuo over oil of vitriol, and in the dark, in crystalline granules and laminæ. — The salt is very readily decomposed by light. When heated on a sheet of paper, it detonates violently, giving off the same odour as terchloracetic acid when it evaporates, and leaves vegetations of pure chloride of silver. If it be moistened with alcohol and the alcohol set on fire, it decomposes more quietly, and without projection (Dumas).

	Crystallized.		Dumas.	Kolbe.	Leblanc.
Ag	108·0	39·97	39·99	39·6	39·80*
4 C	24·0	8·88	8·95	8·9	9·05
3 Cl	106·2	39·31			
4 O	32·0	11·84			
H			0·08		0·10
$C^4Cl^3AgO^4$	270·2	100·00			

* In Fel. Leblanc's memoir (*N. Ann. Chim. Phys.* 10, 199), the proportion of silver is given as 29.80 p.c., doubtless by a misprint.

chlorine and dichloride of carbon, C^4Cl^2, are obtained (Regnault, VIII, 160). — 2. It does not burn when heated alone in the air; but in the flame of a spirit-lamp it burns with a bright yellow flame, forming hydrochloric acid (Faraday). — 3. When its vapour, mixed with hydrogen gas, is passed through a red-hot tube, it is resolved, with evolution of heat and light, into hydrochloric acid gas and a deposit of charcoal. Electric sparks repeatedly passed through the mixture produced the same decomposition (Faraday). — 4. Detonating gas loaded with vapour of chloride of carbon and exploded by the electric spark, is resolved into carbonic oxide and hydrochloric acid gas (Faraday):

$$C^4Cl^4 + 4HO = 4CO + 4HCl.$$

Every 1 vol. hydrogen is replaced by 1 vol. carbonic oxide and 2 vol. hydrochloric acid gas (Faraday). — 5. Vapour of protochloride of carbon passed over red-hot baryta, yields, with vivid combustion, chloride of barium, carbonic acid [carbonate of baryta?], and a small quantity of charcoal (Faraday). — 6. Exposed to the sun in contact with dry chlorine gas, it is converted into C^4Cl^6 (Faraday), but beneath a layer of water it forms terchloracetic acid together with this compound (Kolbe, p. 209). Sulphide of carbon, CS^2, may be converted by the action of chlorine at a red heat into C^2Cl^4; this by ignition into C^4Cl^4; this by chlorine and water, into terchloracetic acid; and this acid, by potassium-amalgam, into acetic acid: hence acetic acid may be formed from sulphide of carbon (Kolbe).

Protochloride of carbon is not decomposed by nitric, sulphuric and hydrochloric acid, and is not soluble in either of these acids (Faraday).

Combinations. Protochloride of carbon is insoluble in water, aqueous acids and aqueous alkalis (Faraday).

At ordinary temperatures, it dissolves *Iodine* with a fine red colour, but without further alteration (Faraday).

With *Bromine* in sunshine it solidifies in a few seconds, forming the crystalline compound C^4Cl^4,Br^2 (Malaguti).

It absorbs *Chlorine gas* abundantly, acquiring a yellow colour: the loose compound thus formed remains unaltered in diffused daylight; but in sunshine it becomes decolorized, and passes into the more intimate crystalline compound C^4Cl^6 (Faraday).

Protochloride of carbon dissolves in *Alcohol*, in *Ether*, and in *Oils* both *fixed* and *volatile* (Faraday).

Perchlorinated Vinic Ether. $C^4Cl^5O = C^4Cl^4,ClO = C^4Cl^3O,Cl^2$.

Regnault. *Ann. Chim. Phys.* 71, 392; also *Ann. Pharm.* 33, 27; also *J. pr. Chem.* 19, 268.

Malaguti. *Compt. rend.* 19, 577, and 21, 749. — *N. Ann. Chim. Phys.* 16, 5; abstr. *Ann. Pharm.* 56, 268; abstr. *J. pr. Chem.* 37, 414.

Chloräther, Perchloräther, Perchlorvinäther, Chlorure de Chloroxéthose (Malaguti); *Oxalaciquinquechlorid* (Berzelius). [Considered as C^4Cl^4,ClO: *Nakavinok;* as C^4Cl^3O,Cl^2: *Kevinikan.*] Discovered by Regnault in 1830.

Formation. By the continued action of chlorine on vinic ether in sunshine (VIII, 184).

Preparation. Dry chlorine gas is continuously passed through ether, which has been freed from alcohol and water by distillation over chloride of calcium, and is contained in a flask, which, for the first 12 hours, is kept at a medium temperature by immersion in water (if it be too much cooled, the hydrochloric ether formed at the same time does not escape, and the chlorovinic ether becomes contaminated with the substitution-products formed by the action of chlorine upon hydrochloric ether); then taken out and exposed to the sun. The yellow liquid after a while deposits numerous crystals of perchlorinated ether, and an additional quantity on subsequent cooling; the decanted mother-liquid exposed to the sun in bottles filled with chlorine, still yields a further crop. All these crystals must be pressed between paper, and dissolved in boiling alcohol. The alcohol as it cools first deposits drops of oil, which harden as they become colder, and then crystalline laminæ of pure perchlorinated ether (Regnault).

Properties. Crystalline laminæ, very much like those of sesquichloride of carbon. Melts at 19° (Regnault). Regular octohedrons of sp. gr. 1·900 at 14·5 (Malaguti). After being heated to 280°, at which temperature it does not boil, it does not solidify till it has been removed from the fire for some hours, probably because it is brought by the heat into another isomeric state. Smells of sesquichloride of carbon and of chloral (Regnault).

				Regnault.
4 C	24	11·48		11·61
5 Cl	177	84·69		84·41
O	8	3·83		3·98
C^4Cl^5O	209	100·00		100·00

The rational formula is probably C^4Cl^3O,Cl^2; for the compound may be prepared from C^4Cl^3O by the action of chlorine gas in sunshine.

Decompositions. 1. The ether when heated to 300°, is comptetely resolved, with ebullition, into chloraldehyde and sesquichloride of carbon, which pass over as an odorous liquid and a crystalline product, the residue remaining colourless to the last trace (Malaguti):

$$2C^4Cl^5O = C^4Cl^4O^2 + C^4Cl^6.$$

In this distillation, 200 parts of the ether yield 56·54 pts of susquichloride of carbon (Malaguti). Calculation (2·209 : 236·4 = 100 : x) gives 56·56, which is almost exactly the same. — Dry chlorine gas exerts no action at 100°, even in the course of several hours; nitric and hydrochloric acid are likewise inactive. — 2. Oil of vitriol acts very slowly when heated; at 240°, it produces ebullition, and evolves, first chloraldehyde, then pungent, cloudy vapours, doubtless consisting of chloraldehyde, hydrochloric acid, and anhydrous sulphuric acid, which, when passed into water, yield chloracetic, hydrochloric, and sulphuric acids. The undecomposed ether remaining in the retort, solidifies after a while on cooling (Malaguti):

$$C^4Cl^5O + HO,SO^3 = C^4Cl^4O^2 + HCl + SO^3.$$

3. Ammoniacal gas does not act on perchlorinated vinic ether, either dissolved in alcohol or in the melted state, unless it be heated sufficiently to form chloraldehyde, in which case this latter compound and the am-

monia form chloracetamide and sal-ammoniac (Malaguti). — 4. The ether distilled with alcoholic potash yields a liquid product (Regnault). The presence of the alcohol complicates the reaction. Even when the mixture is boiled for some time, nothing but pure alcohol passes over; the residue deposits only a small quantity of chloride of potassium, and yields on cooling crystals of undecomposed perchlorinated vinic ether, while the mother-liquor contains a small quantity of formiate of potash. Perhaps a portion of the ether may be converted, first into chloracetic acid, then into chloroform, and lastly into formic acid (Malaguti). — 5. An alcoholic solution of sulphide of potassium decomposes the ether, when heated, yielding chloroxethose, chloride of potassium, and sulphur:

$$C^4Cl^5O + 2KS = C^4Cl^5O + 2KCl + 2S.$$

5 parts of the ether heated with an alcoholic solution of 3 pts. sulphide potassium, produce turbidity from deposition of chloride of potassium, as soon as the action begins; the liquid, when boiled, assumes a dark brown-red colour, and deposits more chloride of potassium; when the liquid is left over night, this deposit increases and becomes covered with laminæ of sulphur; and the decanted liquid mixed with water deposits the oily compound C^4Cl^5O (Malaguti). — 6. Potassium does not act at temperatures many degrees below 300°, but near that temperature, it produces, even in small quantities, a violent explosion (Malaguti).

Chloraldehyde. $C^4Cl^4O^2$.

Malaguti. *N. Ann. Chim. Phys.* 16, 5; abstr. *Compt. rend.* 19, 577; also *J. pr. Chem.* 37, 414: — *Compt. rend.* 21, 445.
Cloez. *N. Ann. Chim. Phys.* 17, 309.

Chloraldehyd, Aldehyde Chloré [*Nevinok*]. — Discovered by Malaguti in 1844.

Formation. — When dry chlorine gas is passed through anhydrous vinic ether exposed to the summer sun, sesquichloride of carbon and chloraldehyde are often formed instead of perchlorinated vinic ether (VIII, 184). — Perchlorinated ether is likewise resolved by distillation into sesquichloride of carbon and chloraldehyde (Malaguti). — 2. Perchlorinated acetic ether, $C^8Cl^8O^4$, repeatedly passed through a tube heated to 400°, and filled with fragments of glass, is converted into chloraldehyde (Malaguti). $C^8Cl^8O^4 = 2C^4Cl^4O^2$. — Even when dry chlorine gas is passed through dry acetic ether, first in daylight and afterwards in sunshine, chloraldehyde is formed as well as septichloracetic ether $C^8HCl^7O^4$ (Cloez).

Preparation. Chlorine gas is passed for 12 hours (as in Regnault's method of preparing perchlorinated vinic ether), through ether, previously freed from alcohol and water by repeated distillation over chloride of calcium, and kept cool by immersion in cold water; the cold water then removed; the liquid exposed to the sun; and the passage of the chlorine continued as long as any action takes place. The product is either sesquichloride of carbon and chloraldehyde, or perchlorinated vinic ether. In the former case, the liquid must be subjected to repeated fractional distillation, so that the less volatile sesquichloride of carbon may remain more and more behind, the process being repeated till the

distillate dissolves in water without the slightest turbidity. If perchlorinated vinic ether has been formed, it is decomposed by distillation into sesquichloride of carbon and chloraldehyde, which are then separated by repeated distillation, as above (Malaguti).

Properties. Transparent, colourless liquid, of sp. gr. 1·603 at 18°. Boils at 118°. Vapour density 6·32. When exposed to the air, it gives off vapours having an intolerably pungent odour. Placed upon the tongue, it first produces dryness, then a white spot, and ultimately exerts a caustic action. Reddens litmus after a few seconds.

		Malaguti.			Vol.	Density.
4 C	24·0	13·22	12·78	C-vapour	4	1·6640
4 Cl	141·6	77·97	77·92	Cl-gas	4	9·8172
2 O	16·0	8·81	9·30	O-gas	1	1·1093
$C^4Cl^4O^2$	181·6	100·00	100·00	Vapour of $C^4Cl^4O^2$	2	12·5905
					1	6·2952

Decompositions. 1. Chloraldehyde sinks in water, and afterwards dissolves in it in the form of hydrochloric and terchloracetic acids. Similarly, with aqueous solutions of the fixed alkalis, it forms a chloride and a terchloracetate (Malaguti):

$$C^4Cl^4O^2 + 2HO = HCl + C^4Cl^3HO^4.$$

2. With gaseous ammonia it becomes heated and immediately solidifies to a mixture of chloracetamide and sal-ammoniac, separable by ether, which dissolves only the chloracetamide. Aqueous ammonia yields the same products (Malaguti):

$$C^4Cl^4O^2 + 2NH^3 = C^4NH^2Cl^3O^2 + NH^4Cl.$$

3. With phosphuretted hydrogen gas it yields a compound (chloracethypide), analogous to chloracetamide, together with hydrochloric acid (Cloez):

$$C^4Cl^4O^2 + PH^3 = C^4PH^2Cl^3O^2 + HCl.$$

4. With a small quantity of alcohol, it becomes heated to the boiling point; if the chloraldehyde be gradually added to excess of alcohol, less heat is evolved, and together with the hydrochloric acid, terchloracetic ether is formed, which is precipitated as an oil by water (Malaguti):

$$C^4Cl^4O^2 + C^4H^6O^2 = C^8H^5Cl^3O^4 + HCl.$$

Bromochloride of Carbon. C^4Cl^4,Br^2.

MALAGUTI (1844). *Compt. rend.* 19, 579; also *N. Ann. Chim. Phys.* 16, 14.

Bromchlorokohlenstoff, Bromure de Chloroxéthose [*Mevinok*].

Protochloride of carbon exposed to sunshine in contact with bromine, solidifies in a few seconds to a crystalline mass, which may be purified by repeated crystallization from alcohol.

The crystals resemble those of sesquichloride of carbon; have a sp. gr. of 2·3 at 21°; taste slightly aromatic; begin to volatilize at 100°;

decompose at about 200° into bromine and protochloride of carbon; and when treated with protosulphide of potassium, are resolved into bromide of potassium and protochloride of carbon (Malaguti):

$$C^4Cl^4Br^2 + 2KS = C^4Cl^4 + 2KBr + 2S.$$

Calculation according to Malaguti.

4 C	24·0	.....	7·37
4 Cl	141·6	.....	43·49
2 Br	160·0	.....	49·14
$C^4Cl^4Br^2$	325·6	.....	100·00

Sesquichloride of Carbon. $C^4Cl^6 = C^4Cl^4,Cl^2$.

FARADAY. In the memoir cited on page 214.

REGNAULT. *Ann. Chim. Phys.* 69, 165.—71, 371; also *Ann. Pharm.* 33, 323; also *J. pr. Chem.* 19, 206.

Anderthalb-Chlorkohlenstoff, Kohlensuperchlorür, Perchloride de Carbone, Chlorure de Chlorèthose (Laurent), [*Kevinok*].

Formation. 1. By the action of chlorine gas in excess on protochloride of carbon in sunshine (Faraday):

$$C^4Cl^4 + Cl^2 = C^4Cl^4,Cl^2.$$

2. By the action of excess of chlorine on chloride of ethylene in sunshine, or more slowly in diffused daylight (Faraday), or with the aid of heat (Liebig):

$$C^4H^4,Cl^2 + 8Cl = C^4Cl^6 + 4HCl.$$

3. By the action of excess of chlorine on hydrochloric ether, first in the shade, afterwards in sunshine (Laurent, *Ann. Chim. Phys.* 64, 328; also *J. pr. Chem.* 11, 423):

$$C^4H^5Cl + 10Cl = C^4Cl^6 + 5HCl.$$

Similarly by the action of excess of chlorine on monochlorinated, bichlorinated, or terchlorinated hydrochloric ether (Regnault, *Ann. Chim. Phys.* 69, 165).

Chloride of ethylene treated alternately with alcoholic potash, which produces each time 1 At. chloride of potassium and 1 At. water, then with chlorine, of which 2 At. are each time taken up, then again with alcoholic potash, then again with chlorine, &c. &c., passes by the following stages into C^4Cl^6:

$$C^4H^4Cl^2 + KO = KCl + HO + C^4H^3Cl. \quad — \quad C^4H^3Cl + Cl^2 = C^4H^3Cl^3$$
$$C^4H^3Cl^3 + KO = KCl + HO + C^4H^2Cl^2. \quad — \quad C^4H^2Cl^2 + Cl^2 = C^4H^2Cl^4$$
$$C^4H^2Cl^4 + KO = KCl + HO + C^4HCl^3. \quad — \quad C^4HCl^3 + Cl^2 = C^4HCl^5$$
$$C^4HCl^5 + KO = KCl + HO + C^4Cl^4. \quad — \quad C^4Cl^4 + Cl^2 = C^4Cl^6.$$

Among these compounds, C^4HCl^3 is the only one which is not accurately known (Regnault, *Ann. Chim. Phys.* 69, 151; also *J. pr. Chem.* 18, 80).

Similarly, hydrochloric ether, C^4H^5Cl, in the course of its transformation by chlorine, by continued replacement of each 1 At. H by 1 At. Cl,

yields the following compounds isomeric with those which are obtained from chloride of ethylene: $C^4H^4Cl^2$; $C^4H^3Cl^3$; $C^4H^2Cl^4$; and C^4HCl^5; and is also finally converted into C^4Cl^6, perfectly identical with the C^4Cl^6 obtained from chloride of ethylene (Regnault).

4. By the action of chlorine on sulphurous ether in sunshine (Ebelmen & Bouquet, *N. Ann. Chim. Phys.* 17, 69).

5. Ether exposed to excess of chlorine in sunshine is converted, sometimes into sesquichloride of carbon and chloraldehyde, sometimes into perchlorinated vinic ether (p. 216), which, however, is afterwards resolved by distillation into sesquichloride of carbon and chloraldehyde (Regnault, Malaguti).

Preparation. Chloride of ethylene is exposed to the sun in a bottle filled with chlorine; water frequently added in small quantities to absorb the resulting hydrochloric acid gas; the chlorine frequently renewed as long as it exhibits any alteration; the resulting crystals washed with water to remove the greater part of the hydrochloric acid; pressed between paper; heated to sublimation; and the sublimate dissolved in alcohol, precipitated from the alcoholic solution by water containing potash to remove the last traces of hydrochloric acid, then washed with water, pressed between bibulous paper, and dried in vacuo over oil of vitriol (Faraday). — The chloride of ethylene may also be heated nearly to the boiling point, and chlorine gas uninterruptedly passed through it as long as hydrochloric acid continues to form, whereby, however, not the whole, but only the greater part of the chloride of ethylene is converted into sesquichloride of carbon, which crystallizes out for the most part when the liquid is artificially cooled (Liebig, *Ann. Pharm.* 1, 219).

2. A small quantity of hydrochloric ether is introduced into a bottle filled with dry chlorine gas, and set aside in the shade for 24 hours; after which the chlorine is renewed, and the vessel exposed to the sun; at the commencement of the process, such exposure would produce explosion (Laurent). — Or, more advantageously: Alcohol is heated with concentrated hydrochloric acid, the evolved vapour of hydrochloric ether passed through water and oil of vitriol to purify it, and then brought in contact with chlorine in a bottle exposed to the summer sun (Regnault).

3. Perchlorinated vinic ether is decomposed by distillation into sesquichloride of carbon and chloraldehyde, and the distillate repeatedly treated with water, which takes up chloraldehyde in the decomposed state, and leaves chloride of carbon (Malaguti, *N. Ann. Chim. Phys.* 16, 6, and 14).

Properties. Transparent, colourless crystals, often united in arborescent tufts (Faraday). Right rhombic prisms belonging to the right prismatic system. (*Fig.* 65, with p-face) $u : a = 122°$; $u' : t = 119°$; $p : i = 119° 40'$; $i : t = 150° 20'$; no cleavage-planes (Brooke, *Ann. Phil.* 23, 364); $u : t = 119° 30'$; $i : t = 150° 30'$ (Laurent, *Rev. scient.* 9, 33). — Refracting power = 1·5767. Sp. gr. about = 2·00. As hard as sugar, easily pulverized, and then appears like pounded sugar. Does not conduct electricity. Melts at 160° and boils at 182°, subliming in the crystalline form, but volatilizes in the air even at ordinary temperatures (Faraday). Vapour-density = 8·157 (Regnault). Smells strongly aromatic and like camphor; taste scarcely perceptible (Faraday).

			Regnault (2).	Richardson.	Malaguti (3).
4 C	24·0	10·15	10·15	10·42	10·00
6 Cl	212·4	89·85			90·11
C^4Cl^6	236·4	100·00			100·11

Faraday likewise found in the compound 3 At. Cl to 2 At. C.

Decompositions. 1. Sesquichloride of carbon is resolved by repeated distillation, or by once passing its vapour through a red-hot tube, into protochloride of carbon and chlorine gas, part of which is absorbed by the former and gives it a yellow colour (Faraday). — 2. In the flame of a spirit-lamp it burns with a red flame, producing hydrochloric acid, but goes out when removed from the lamp-flame. In oxygen gas it may be set on fire without admixture with any other substance, and sometimes burns with splendour. Its vapour mixed with oxygen gas is not set on fire by electric sparks, even at 200°; but in a red-hot tube the mixture is resolved into carbonic acid, carbonic oxide, and phosgene gases (Faraday.)

3. Melts at a moderate heat when mixed with iodine, and at a higher temperature, gives up to 2 At. chlorine to that body, yielding protochloride of carbon and chloride of iodine. Sulphur and phosphorus act in a similar manner (Faraday). — 4. Its vapour mixed with hydrogen gas is not set on fire by the electric spark, even at 200°; but, when passed through a red-hot tube, it deposits charcoal and forms hydrochloric acid gas. (Faraday). — 5. Nearly all metals heated in its vapour are converted into chlorides, with separation of charcoal; potassium exhibits vivid combustion.

6. The vapour passed over red-hot baryta, strontia or lime (magnesia has no action), forms, with evolution of light and heat and deposition of charcoal, a chloride of the metal and a carbonate of the alkali; with heated oxide of lead, it forms chloride of lead, together with carbonic acid and carbonic oxide gases; with oxide of zinc it yields similar products, sometimes with the addition of phosgene gas; with stannic, cupric, and mercuric oxides, and with peroxide of lead, it yields nothing but a metallic chloride and carbonic acid gas (Faraday). — 7. Sesquichloride of carbon heated, even but slightly, with an alcoholic solution of sulphide of hydrogen and potassium, gives off sulphuretted hydrogen with violence, and yields a deposit of chloride of potassium; but if subsequently distilled, it gives off a mixture of alcohol and protochloride of carbon, and leaves a residue consisting of chloride of potassium and a brown substance (Regnault; for the equation, *vid.* p. 215). — Water extracts chloride of potassium from the residue, forming, however, a brown solution, which is decolorized by hydrochloric acid, with precipitation of a small quantity of brown, viscid, very stinking matter; the portion not dissolved by the water is a dark brown substance likewise insoluble in alcohol, which when distilled, behaves like a mixture of sulphur and charcoal, products perhaps arising from the decomposition having gone too far. An alcoholic solution of sulphide of potassium behaves exactly like sulphide of hydrogen and potassium, excepting that an excess of it heated with sesquichloride of carbon yields other and very complicated products (Regnault).

8. Sesquichloride of carbon does not absorb ammoniacal gas in the cold, but is decomposed by it when heated (Bineau, *Ann. Chim. Phys.* 70, 270).

Sesquichloride of carbon exhibits no decomposition when heated with charcoal, nitric acid, sulphuric acid, aqueous ammonia, potash or soda, and its solutions in nitric acid or alcohol do not precipitate nitrate of silver (Faraday).

Combinations. Sesquichloride of carbon dissolves very sparingly in *Water*, and not more abundantly in aqueous alkalis (Faraday).

It dissolves in boiling *Nitric acid*, and separates therefrom partly on cooling, partly on the addition of water (Faraday).

It dissolves in *Alcohol*, is precipitated therefrom by water; more abundantly in *Ether;* also in *Oils*, both *fixed* and *volatile* (Faraday).

e. Oxychlorine-nucleus. C^4Cl^3O.

Chloroxethose. C^4Cl^3O.

Malaguti (1844). *N. Ann. Chim. Phys.* 16, 19; abstr. *Compt. rend.* 19, 579.

Chloroxăthos, Chloroxéthose [*Vinikan*].

Formation. From perchlorinated vinic ether and protosulphide of potassium (p. 218).

Preparation. 16 pts. of perchlorinated vinic ether are boiled with a solution of 50 pts. protosulphide of potassium in 200 pts. of 95 per cent alcohol, till the ether is dissolved; the liquid decanted on the following day from the deposited chloride of potassium, and diluted with water; the oil, which sinks to the bottom after a while, and still contains undecomposed perchlorinated ether, again heated with a solution of 25 pts. protosulphide of potassium in 100 pts. alcohol; precipitated again with water; finally freed from admixed sulphur by boiling with aqueous potash and from an alliaceous-smelling substance by boiling with nitric acid; then washed with a large quantity of water, dried in vacuo, rectified two or three times, and once more washed and dried. It is best kept under water.

Properties. Transparent, colourless oil of sp. gr. 1·652 at 21°. Boils at 210°. Becomes coloured thereby, and leaves a scanty black residue; but the distillate after washing consists of pure chloroxethose. Has a very agreeable odour, like that of the flowers of *Spiræa Ulmaria*.

			Malaguti.
4 C	24·0	17·37	17·18
3 Cl	106·2	76·84	76·63
O	8·0	5·79	6·19
C^4Cl^3O	138·2	100·00	100·00

Decompositions. Chloroxethose when kept in vessels containing air loses its agreeable odour, and becomes sour and fuming. — It is decomposed by hot nitric acid of sp. gr. 1·5, with formation of carbonic acid. — Weak nitric acid and alkalis exert no action on chloroxethose.

When exposed to sunshine in dry chlorine gas, it forms crystals in a

few days, and after the excess of chlorine has been expelled, solidifies completely as perchlorinated vinic ether. In presence of water, terchloracetic acid and hydrochloric are formed, together with perchlorinated vinic ether and a small quantity of sesquichloride of carbon, inasmuch as the perchlorinated vinic ether, at the moment of its formation, is resolved by water into the two first mentioned products:

$$C^4Cl^3O + 3HO = C^4Cl^3HO^4 + 2HCl.$$

In a similar manner, chloroxethose exposed to the sun gradually takes up 2 At. bromine, and forms the crystalline compound C^4Cl^3O,Br^2.

Chloroxethose is insoluble in water, but dissolves in alcohol and in ether (Malaguti).

Bromide of Chloroxethose. C^4Cl^3O,Br^2.

Malaguti (1814). *N. Ann. Chim. Phys.* 16, 25; abstr. *Compt. rend.* 19, 579.

Brom-Chloroäthos, Bromure de Chloroxethose, [*Mevinikan*].

Chloroxethose exposed to the sun in contact with bromine, solidifies in a few days in the crystalline state. By recrystallization from alcohol, crystals are obtained, having the form of sesquichloride of carbon, and a sp. gr. of 2·5 at 18°. They melt at 96°, and are resolved at 180° into bromine and chloroxethose. With an alcoholic solution of protosulphide of potassium, they yield bromide of potassium and chloroxethose, and in their other chemical relations, exhibit the closest resemblance to perchlorinated vinic ether, C^4Cl^3O,Cl^2 (Malaguti).

				Malaguti.
4 C	24·0	....	8·05	..... 7·99
3 Cl	106·2	....	35·61	
2 Br	160·0	....	53·66	
O	8·0	....	2·68	
$C^4Cl^3Br^2O$	298·2	....	100·00	

100 pts. of the compound yield 270 pts. chloride of silver + bromide of silver (Malaguti).

ζ. *Phosphochlorine-nucleus.* $C^4(PH^2)Cl^3$.

Chloracetyphide. $C^4(PH^2)Cl^3O^2 = C^4(PH^2)Cl^3,O^2$.

Cloez (1846). *N. Ann. Chim. Phys.* 17, 309.

Produced when phosphuretted hydrogen gas is passed through chloraldehyde, its formation being attended with evolution of hydrochloric acid gas:

$$C^4Cl^4O^2 + PH^3 = C^4(PH^2)Cl^3O^2 + HCl.$$

Also by passing the same gas through perchlorinated formic ether, phosgene being produced at the same time:

$$C^6Cl^6O^4 + PH^3 = C^4(PH^2)Cl^3O^2 + 2CClO + HCl.$$

Small, white, loose crystalline scales, having a slightly alliaceous odour and bitterish taste.

When heated in the air, it leaves phosphoric acid mixed with charcoal.

Insoluble in water, sparingly soluble in wood-spirit, alcohol, and ether (Cloez).

η. Sulphochlorine-nucleus. C^4ClH^2S.

Chlorosulphuretted Ether. $C^4H^2ClSO = C^4ClH^2S,HO = C^4OSClH,H^2$.

Malaguti (1839). *Ann. Chim. Phys.* 70, 354; also *Ann. Pharm.* 32. 29.

Sulfochlorvinäther, Ether chlorosulfuré.

Preparation (p. 184).

Yellowish crystalline scales, greasy to the touch, and having an offensive odour, melting at 70° to 72°, and solidifying to a soft, laminated crystalline mass.

Decomposed by alcoholic potash into sulphide of potassium, chloride of potassium, and acetate of potash:

$$C^4H^2ClSO + 3KO = KS + KCl + C^4H^3KO^4.$$

Insoluble in water, but soluble in alcohol and ether (Malaguti).

					Malaguti.
4 C	24·0	....	27·78	.....	27·58
3 H	3·0	....	3·47	.....	3·59
Cl	35·4	....	40·97	.....	41·11
S	16·0	....	18·52	.....	18·90
O	8·0	....	9·26	.....	8·82
C^4H^2ClSO	86·4	....	100·00	.....	100·00

Conjugated Compounds of the Chlorine-nuclei.

Bichlorocarbonic Ether. $C^5Cl^2H^5O^3 = C^4Cl^2H^5O,CO^2$.

Cahours (1843). *N. Ann. Chim. Phys.* 9, 203; also *Ann. Pharm.* 47, 293; also *J. pr. Chem.* 30, 242.

Bichlorkohlenvinester, Doppeltchlorkohlensäureäther, Ether carbonique bichloruré.

Carbonic ether, C^4H^5O, CO^2, is saturated by daylight with dry chlorine gas, and heated on the water-bath to 70°—80° in the latter part of the process; and as soon as the chlorine ceases to act, the excess of that gas is expelled at 70° to 75° by a stream of carbonic acid gas.

Colourless liquid, much heavier than water, and of sweet, peculiar odour.

Decomposes when boiled. Not altered by chlorine in daylight even

in a month; but in sunshine it is converted thereby into perchlorocarbonic ether and hydrochloric acid (Cahours):

$$C^5Cl^2H^3O^3 + 6Cl = C^5Cl^5O^3 + 3HCl.$$

Insoluble in water, but soluble in alcohol (Cahours):

			Cahours.
5 C	30·0	23·47	23·34
3 H	3·0	2·35	2·41
2 Cl	70·8	55·40	55·48
3 O	24·0	18·78	18·77
$C^5Cl^2H^3O^3$	127·8	100·00	100·00

Perchlorocarbonic Ether. $C^5Cl^5O^3 = C^4Cl^5O,CO^2$.

CAHOURS. *N. Ann. Chim. Phys.* 9, 203; also *Ann. Pharm.* 47, 294; also *J. pr. Chem.* 30, 243.
MALAGUTI. *N. Ann. Chim. Phys.* 16, 30; abstr. *J. pr. Chem.* 37, 426.

Chlorocarbonic Ether, Perchlorkohlenvinester, Ueberchlorkohlensäureäther, Ether carbonique perchloruré, Ether chlorocarbonique. — Discovered by Cahours in 1844.

Preparation. Dry chlorine gas is passed continuously in sunshine through bichlorocarbonic ether, till, after 2 or 3 days, the whole solidifies to a crystalline mass, which is then quickly pressed between paper, and dried in vacuo (Cahours). The product cannot be purified by leaving it to crystallize from alcohol or ether, because it is thereby partly decomposed and converted into a viscid mass (Cahours).

Properties. Small snow-white needles, which melt when heated, and solidify again in the crystalline state on cooling (Cahours). Melts between 85° and 86°, and solidifies between 65° and 63° (Malaguti). Has a faint odour (Cahours):

			Cahours.
5 C	30	12·99	13·19
5 Cl	177	76·62	76·69
3 O	24	10·39	9·91
H			0·21
$C^5Cl^5O^3$	231	100·00	100·00

Decompositions. 1. When this compound ether is distilled, part of it goes over undecomposed, the rest in the form of carbonic acid gas, chloraldehyde and sesquichloride of carbon (Malaguti):

$$2C^5Cl^5O^3 = 2CO^2 + C^4Cl^4O^2 + C^4Cl^6.$$

2. When part of the ether is heated with 4 pts. of hydrate of potash, and 12 pts. water, a violent action sets in as soon as the liquid begins to boil, and continues till all the ether has disappeared, and is resolved into chloride of potassium, carbonate of potash, and formiate of potash (Malaguti):

$$C^5Cl^5O^3 + 9KO + HO = 5KCl + 3(KO,CO^2) + C^2HKO^4.$$

If only half the above quantity of potash be used, the decomposition

goes on but slowly even at a boiling heat, and when half the ether has disappeared, the same products are found in the liquid (Malaguti).

3. Perchlorocarbonic ether exposed at ordinary temperatures to a stream of ammoniacal gas, absorbs that gas and becomes warm and soft; if it be warmed from without, after being saturated with ammonia, it becomes very hot, gives off a large quantity of very thick smoke, but not a trace of water, and hardens to a brown mass consisting of chlorocarbethamide, sal-ammoniac, another ammoniacal salt [chlorocarbethamate of ammonia ?] and a small quantity of a black powder resembling paracyanogen (Malaguti). — Vinic ether leaves the sal-ammoniac and paracanoygen undissolved, and when evaporated yields the chlorocarbethamide, while the other ammoniacal salt remains in the mother-liquor. On evaporating and cooling the mother-liquor, the last-mentioned salt is obtained in the form of a white, fibrous, easily fusible, very bitter mass, which dissolves very easily in water, alcohol, and ether, gives off ammonia with cold potash, and, though it contains chlorine, does not precipitate a solution of silver when dissolved in water containing acetic acid (Malaguti). — [Chlorocarbethamide, in consequence of the uncertainty still existing with regard to its constitution, is described only in the form of an appendix (p. 228.) If we suppose that the essential products of the decomposition are sal-ammoniac, chlorocarbethamide, and chlorocarbethamate of ammonia, and assign to the latter the formula proposed by Gerhardt, the equation may be :

$$6C^5Cl^5O^3 + 20NH^3 = 2C^{10}N^3H^6Cl^7O^4 + C^{10}N^3H^{12}Cl^7O^{10} + 9NH^4Cl + 2N.$$

According to this equation, nitrogen should be evolved at the same time.]

Perchlorocarbonic ether thrown by small portions into aqueous ammonia, makes a loud hissing noise like red-hot iron, and forms, with great evolution of heat, a thin crystalline magma, which leaves chlorocarbethamide on the filter; the brown filtrate evaporated and exhausted with ether, resolves itself into an insoluble residue of sal-ammoniac, carbonate of ammonia, formiate of ammonia, and a brown substance, and a solution of chlorocarbethamate of ammonia (p. 229) (Malaguti). Hence aqueous ammonia forms, not merely an amide, like ammoniacal gas, but likewise carbonic and formic acid, like potash (Malaguti).

4. Perchlorocarbonic ether dissolves in alcohol, with rise of temperature amounting to only a few degrees, and forms a very acid, spontaneously fuming liquid, from which water throws down a heavy, oily mixture of carbonic ether, terchloracetic ether, and perchlorocarbonic ether, having an aromatic taste and smell, while hydrochloric acid (together with a small quantity of terchloracetic acid) remains in solution (Malaguti):

$$C^5Cl^5O^3 + 2C^4H^6O^2 = C^5H^5O^3 + C^3H^5Cl^3O^4 + 2HCl.$$

The composition of the oil precipitated by water is determined by the following reactions. When shaken up with aqueous ammonia, the greater part of it dissolves, with great evolution of heat. The solution decanted from the undissolved oil, which is carbonic ether, gradually becomes turbid and deposits chloroform as an oil, while carbonate and hydrochlorate of ammonia, together with other ammoniacal salts containing chlorine, remain in solution. The terchloracetic ether has indeed been converted by the ammonia successively into chloracetamide, terchloracetate of ammonia, chloroform, and carbonate, hydrochlorate, and formiate of ammonia. — Ammoniacal gas makes the oil hot, and converts it into a white solid mass, which, besides an oil and sal-ammoniac, likewise contains chlorocarbethamide, showing that undecomposed perchlorocarbonic ether is present in the oil (Malaguti).

Appendix to Perchlorocarbonic Ether.

1. Chlorocarbethamide. $C^{10}N^3H^6Cl^7O^4 = C^{10}Ad^3Cl^7O^4$?

Formation (p. 227). — Formed likewise in a similar manner from chlorosuccinic ether and ammoniacal gas.

Preparation. Perchlorocarbonic ether is saturated in the cold with dry ammoniacal gas, the mass carefully heated till it gives off dense fumes and solidifies to a brown mass; this mass pressed between bibulous paper and exhausted with anhydrous ether; and the yellow filtrate left to evaporate, whereupon impure chlorocarbethamide separates in loose, yellowish, unctuous laminæ. These are pressed between paper to free them from an oily substance, dissolved in boiling water, and decolorized by a small quantity of animal charcoal; the filtrate cooled to the crystallizing point; and the resulting white laminæ purified by recrystallization, till they taste sweet, and have lost their bitter aftertaste; in this process however, a considerable quantity is lost. 100 pts. of perchlorocarbonic ether yield 20 pts. of crude chlorocarbethamide, and a much smaller quantity of the purified product.

Properties. — White, crystalline scales greasy to the touch; they melt at 138° to 140°, begin to turn brown at 220°, boil at 260°; and when suddenly raised to a high temperature, sublime undecomposed, in specular iridescent laminæ.

Calculation

according to Malaguti.			according to Gerhardt.		
10 C	60·0	15·79	10 C	60·0	15·47
3 N	42·0	11·06	3 N	42·0	10·83
6 H	6·0	1·58	6 H	6·0	1·55
7 Cl	247·8	65·25	7 Cl	247·8	63·90
3 O	24·0	6·32	4 O	32·0	8·25
	379·8	100·00		387·8	100·00

Malaguti

fused

from Perchlorocarbonic Ether.	*from Chlorosuccinic Ether.*
15·41	15·30
10·82	10·50
1·65	1·59
64·97	65·23
7·15	7·38
100·00	100·00

[Malaguti's empirical formula, $C^{10}N^3H^6Cl^7O^3$, contains an uneven number of atoms: hence Gerhardt proposes the formula $C^{10}N^3H^6Cl^7O^4$].

Chlorocarbethamide does not evolve ammonia when triturated in the cold with hydrate of lime, but evolves it when boiled with potash. In aqueous ammonia it dissolves gradually, with formation of crystallizable chlorocarbethamate of ammonia.

It dissolves sparingly in water, readily in alcohol and vinic ether. (Malaguti, *N. Ann. Chim. Phys.* 16, 35 and 73; abstr. *J. pr. Chem.* 37, 426 and 434.)

2. Chlorocarbethamic Acid. $C^{10}NH^6Cl^7O^{10}=C^{10}AdH^4Cl^7O^{10}$?

Known only in the form of an ammoniacal salt. This salt is obtained by digesting chlorocarbethamide with aqueous ammonia. A few days after the solution is complete, the liquid is left to evaporate in vacuo over oil of vitriol, whereby the chlorocarbethamate of ammonia is obtained in white, unctuous, very bitter scales, which melt between 35° and 37°, and dissolve very readily in water, alcohol, and ether.

The salt triturated with hydrate of potash, gives off a large quantity of ammonia. When its aqueous solution supersaturated with baryta-water has ceased to give off ammonia at 90°, it evolves a fresh quantity on boiling (in consequence of the decomposition of the acid containing amidogen), and afterwards exhibits the chlorine-reaction with a solution of silver. The aqueous solution of 100 pts. of the crystallized salt yields with bichloride of platinum a quantity of chloroplatinate of ammonium containing 8·5 pts. of ammonia; hence out of 3 At. N contained in the salt, 2 At. are present in the form of ammonia. Calculation gives only 7·7 to 7·8 pts. of ammonia; but the free hydrochloric acid in the bichloride of platinum used, probably converted a portion of the amidogen contained in the chlorocarbethamic acid into ammonia. (Malaguti, *N. Ann. Chim. Phys.* 16, 35; abstr. *J. pr. Chem.* 37, 434.)

	Calculation according to Malaguti.			according to Gerhardt.			Malaguti. *Crystals.*
10 C	60·0	....	13·83	60·0	....	13·58	..... 13·49
3 N	42·0	....	9·68	42·0	....	9·50	..... 9·72
12 H	12·0	....	2·77	12·0	....	2·72	..... 2·88
7 Cl	247·8	....	57·12	247·8	....	56·09	..... 56·82
9 O	72·0	....	16·60	80·0	....	18·11	..... 17·09
	433·8	....	100·00	441·8	....	100·00	..... 100·00

According to Malaguti = $2NH^4O,C^{10}NH^4Cl^7O^7$, or $2NH^4O,C^{10}NH^2Cl^4O^5+2Aq$.—According to Gerhardt = $2NH^3,C^{10}NH^6Cl^7O^{10}$ [= $2NH^3,C^{10}AdH^4Cl^7O^{10}$; according to this formula, chlorocarbethamic acid would be = $C^{10}AdCl^7H^4O^4,O^6$, or, if the salt contains 4 atoms of water, = $C^{10}AdCl^7,O^6$, or $C^{10}NH^2Cl^7,O^6$].

Chlorovinic Formiate. $C^6H^5ClO^4=C^4ClH^4O,C^2HO^3$.

Dumas (1833). *Ann. Chim. Phys.* 54, 226; also *Ann. Pharm.* 10, 277.
Cloez. *N. Ann. Chim. Phys.* 17, 303.
Cahours. *N. Ann. Chim. Phys.* 19, 346; also *J. pr. Chem.* 40, 427.

Chloroformic Ether, Chlorameisenvinester, Chlorkohlenoxydäther, Ether oxychlorocarbonique (Dumas), *Ether chloroformique* (Cahours).

Formation and Preparation. 1. Thirty grammes of absolute alcohol poured into a bottle containing 15 litres of phosgene gas, cause great evolution of heat, and form an amber-coloured liquid. Air is then admitted into the bottle; the liquid poured out after a quarter of an hour; shaken up with an equal volume of water; set aside; the layer of chloroformic ether below the aqueous hydrochloric acid drawn out with a pipette; and rectified in the water-bath over chloride of calcium and litharge (Dumas):

$$C^4H^6O^2 + 2CClO = C^6H^5ClO^4 + HCl.$$

2. Perchlorovinic formiate $C^6Cl^6O^4$ is dropped into alcohol; water added; and the whole left to itself, whereupon an upper layer of aqueous hydrochloric acid is obtained, and a lower one consisting of a mixture of chloroformic ether and terchloracetic ether. On distilling this mixture, the chlorovinic formiate passes over first, between 95° and 100°; then, at a higher temperature, the terchlorovinic acetate, which must be collected in a separate receiver (Cloez). For the equation, *vid.* p. 233.

3. Strong alcohol is poured by small portions into perchloroxalate of methyl contained in a large, loosely stoppered bottle, as long as each addition causes evolution of heat and effervescence arising from escape of hydrochloric acid gas; the mixture, when cold, is shaken up with excess of water; the very strong smelling oily mixture of chloroformic ether and oxalic ether thereby precipitated, repeatedly washed with water; then digested for 24 hours over chloride of calcium; distilled in a retort provided with a thermometer, the boiling point rising from 92° to 190°; the first portion of the distillate collected apart; and rectified once or twice, till it exhibits a constant boiling point. (Cahours; for the equation, *vid.* p. 177.)

Properties. — Thin, transparent colourless liquid, of sp. gr. 1·133 at 15°. Boils at 94° under a pressure of 0·773 m. Vapour-density = 3·823. Has a tolerably agreeable odour when mixed with a large quantity of air; but in the pure state it is very suffocating and excites a copious flow of tears (Dumas).

			Dumas.	Cahours.
6 C	36·0	33·21	34·2	33·17
5 H	5·0	4·61	5·0	4·72
Cl	35·4	32·66	30·7	32·32
4 O	32·0	29·52	30·1	29·79
$C^6H^5ClO^4$	108·4	100·00	100·0	100·00

	Vol.	Density.
C-vapour	6	2·4960
H-gas	5	0·3465
Cl-gas	1	2·4543
O-gas	2	2·2186
Vapour of $C^6H^5ClO^4$	2	7·5154
	1	3·7577

Decompositions. 1. Chlorovinic formiate burns with a green flame and afterwards precipitates solution of nitrate of silver (Dumas). — 2. It dissolves in oil of vitriol, and soon gives off a large quantity of hydrochloric acid gas, especially when heated; at a higher temperature, the solution blackens and gives off a combustible gas (Dumas). — 3. In contact with warm water it becomes strongly acid (Dumas). — 4. With aqueous ammonia it becomes strongly heated, even to explosive ebullition, and disappears completely, forming urethane and sal-ammoniac, from which latter the urethane may be separated by evaporation in vacuo, and distillation (Dumas):

$$C^6H^5ClO^4 + 2NH^3 = C^6NH^7O^4 + NH^4Cl.$$

5. The ether does not yield alcohol when treated with aqueous potash (Gerhardt, *Ann. Chim. Phys.* 72, 184).

Bichlorovinic Formiate. $C^6H^4Cl^2O^4 = C^4Cl^2H^3O,C^2HO^3$.

MALAGUTI (1839.) *Ann. Chim. Phys.* 71, 369; also *Ann. Pharm.* 32, 39' also *J. pr. Chim.* 18, 52.

Bichloroformic Ether, Bichlorameisenvinester, Chlorameisenäther, Ether formique chloré.

Formic ether through which a stream of chlorine is passed, does not become heated, but begins after two hours to give off hydrochloric acid gas, and on the application of external heat is converted, after about forty hours' passage of the gas, into impure bichloroformic ether, which is then heated for some time in a retort to 90° (at 105°, it would turn brown and decompose), to drive off the more volatile matters; then washed with water, whereupon it diminishes considerably in volume; set aside for some days under water; and lastly dried in vacuo over oil of vitriol and lime.

Transparent, colourless liquid of sp.gr. 1·261 at 16°. Has an aromatic odour, a bitter taste, and reddens litmus slightly.

				Malaguti.
6 C	36·0	25·21		23·97
4 H	4·0	2·80		2·88
2 Cl	70·8	49·58		46·75
4 O	32·0	22·41		26·40
$C^6H^4Cl^2O^4$	142·8	100·00		100·00

Bichloroformic ether decomposes below its boiling point. — It is very slowly decomposed by water, but very easily by aqueous potash, into acetate of potash, formiate of potash, and chloride of potassium:

$$C^6H^4Cl^2O^4 + 4KO = C^4H^3KO^4 + C^2HKO^4 + 2KCl.$$

It dissolves in alcohol and in ether (Malaguti).

Bichloromethylic Acetate.

$C^6H^4Cl^2O^4 = C^2Cl^2HO,C^4H^3O^3 = C^2H^3O,C^4Cl^2HO^3$.

MALAGUTI (1839). *Ann. Chim. Phys.* 70, 379; also *Ann. Pharm.* 32, 47; also *J. pr. Chem.* 18, 59.

Bichloressigformester, Chlorhaltiges essigsaures Methylen, Methylenchloressigäther, Acetate de Methylene chloruré.

Obtained by passing chlorine gas to saturation through methylic acetate, first at the temperature of the air, then at 60°, distilling off the more volatile part of the product till the residue begins to turn brown at 145°; washing it, first with weak potash-ley, then for a considerable time with water; and drying it in vacuo over oil of vitriol and lime.

Transparent, colourless liquid of sp. gr. 1·25; boils between 145° and 148°, but begins to turn brown and give off fumes at 138°. Has a pungent odour like that of acetic acid; tastes sweet at first, but afterwards alliaceous and very burning. Neutral.

				Malaguti.
6 C	36·0	25·21		25·96
4 H	4·0	2·80		3·08
2 Cl	70·8	49·58		48·24
4 O	32·0	22·41		22·72
$C^6H^4Cl^2O^4$	142·8	100·00		100·00

Metameric with bichlorovinic formiate.

Bichloromethylic acetate burns with a yellow flame, green-edged at bottom.—Decomposes slowly with water, quickly with aqueous potash, and violently with alcoholic potash, yielding formic, acetic, and hydrochloric acid. It then disappears completely; nevertheless a volatile pungent matter (likewise found by Laurent in the decomposition of the following compound) is at the same time observed to form, its quantity being greater as the ether is less pure (Malaguti):

$$C^4HCl^2O,C^4H^3O^3 + 4KO = 2KCl + C^2HKO^4 + C^4H^3KO^4.$$

Terchloromethylic Acetate. $C^6H^3Cl^3O^4 = C^2H^3O,C^4Cl^3O^3$.

Laurent (1836). *Ann. Chim. Phys.* 63, 382; also *J. pr. Chem.* 11, 236.

Dumas. *Ann. Chim. Phys.* 73, 85; also *Ann. Pharm.* 32, 111; also *J. pr. Chem.* 17, 206.

Terchloressigformesser, Chloressigsaures Methyloxyd; Chloracetate méthylique (Dumas), *Chloracetate de Chlorométhylase* (Laurent).

Formation and Preparation. 1. Chlorine gas is slowly passed through methylic acetate contained in a Liebig's bulb-apparatus, till hydrochloric acid is no longer evolved. When the saturation is nearly complete, every bubble of chlorine produces a light in the dark, but without any perceptible evolution of heat. The liquid saturated with chlorine yields at first a distillate consisting of two layers, which is set aside; and the residue in the retort is repeatedly distilled till the boiling point becomes constant (Laurent). — 2. Terchloracetic acid is distilled with wood-spirit and a small quantity of oil of vitriol, and the compound ether separated in oily drops from the distillate by addition of water (Dumas).

Properties. Transparent, colourless oil, heavier than water (Laurent, Dumas); boils at 145°, and may be repeatedly distilled without decomposition (Laurent). Has an agreeable odour like that of peppermint (Dumas).

			Laurent.	Dumas.
6 C	36·0	20·32	20·5	21·5
3 H	3·0	1·69	1·7	1·7
3 Cl	106·2	59·93		
4 O	32·0	18·06		
$C^6H^3Cl^3O^4$	177·2	100·00		

Terchloromethylic acetate is readily decomposed by caustic potash; the solution turns brown, gives off a vapour which has a sweet taste and

attacks the eyes, deposits chloromethylase, C^2HCl (p.342) as an oil, and retains chloride of calcium, and probably also formiate of potash in solution (Laurent):

$$C^6H^3Cl^3O^4 + 4KO = C^2HCl + 2KCl + 2C^2HKO^4.$$

It is insoluble in water, but dissolves in alcohol and in ether (Laurent).

Perchloromethylic Acetate = Perchlorovinic Formiate.

$C^6Cl^6O^4 = C^2Cl^3O, C^4Cl^3O^3 = C^4Cl^5O, C^2ClO^3$.

CLOEZ (1845). *N. Ann. Chim. Phys.* 17, 297 ; abstr. *Compt. rend.* 21, 69. — *N. Ann. Chim. Phys.* 17, 311; abstr. *Compt. rend.* 21, 874; abstr. *N. J. Pharm.* 9, 16; abstr. *J. pr. Chem.* 37, 345.

Perchloroformic Ether, Perchloressigformester, Perchlorameisenvinester, Chloressigsaures Chlormethyloxyd, Chorameisensaures Chloräthyloxyd, Acétate de Methylène perchloré, Ether formique perchloré.

Formation and Preparation. 1. Chlorine gas is passed through methylic acetate, till it is no longer absorbed in sunshine, and the product purified in the ordinary way. — 2. Similarly with formic ether (Cloez). — Methylic acetate and vinic formiate have the same empirical formula, viz. $C^6H^6O^4$; but when treated with aqueous potash, the former is resolved into wood-spirit and acetate of potash; the latter into alcohol and formiate of potash : they are therefore metameric. But the compound $C^6Cl^6O^4$ obtained when all the hydrogen of either of these compounds is replaced by chlorine, is exactly the same ; not only in composition and physical properties, but likewise in all its reactions, from whichever compound it may have been prepared. The compound $C^6Cl^6O^4$ appears therefore to have a constitution totally different from that of the two compound ethers, from which it may have been formed. The case is similar with the two isomeric compounds, monochlorinated hydrochloric ether $[C^4H^2Cl^2,H^2]$ and chloride of ethylene $[C^4H^4,Cl^2]$, both of which, when treated with chlorine, are converted into the same compound, viz., sesquichloride of carbon C^4Cl^6 (Cloez). — All perchlorinated compound ethers indeed appear to have a constitution different from that of the ethers from which they have been formed by the action of chlorine; those of the ethylene-series, for example, by no means appear to contain perchlorinated vinic ether C^4Cl^5O: for this compound resists the action of aqueous potash; which on the other hand, when it acts upon any perchlorinated compound ether, exchanges its oxygen for the chlorine of the perchlorinated vinic ether which might be supposed to exist therein. (Malaguti, *N. Ann. Chim. Phys.* 16, 29; also *J. pr. Chem.* 27. 425.)

Properties. Transparent, colourless liquid. Sp. gr. of (1) = 1·691 at 18°; of (2) = 1·705 at 18°. Both boil at about 200°, and when pure volatilize without decomposition, but if impure, leave a carbonaceous residue. Vapour-density of (2) = 9·31. Both (1) and (2) have a suffocating odour, and taste harsh and unpleasant at first, afterwards from decomposition, intolerably acid (Cloez).

		Cloez (1).	Cloez (2).			
6 C	36·0	12·84	13·60	12·9	C-vapour	6 2·4960
6 Cl	212·4	75·75	74·50	74·7	Cl-gas	6 14·7258
4 O	32·0	11·41	11·78	12·4	O-gas	2 2·2186
H			0·12			
$C^6Cl^6O^4$	280·4	100·00	100·00	100·0	Vapour of $C^6Cl^6O^4$	2 19·4404
						1 9·7202

Decompositions. 1. Either (1) or (2) passed through a red-hot tube is resolved into phosgene gas and chloraldehyde:

$$C^6Cl^6O^4 = C^4Cl^4O^2 + 2CClO.$$

2. In contact with water or damp air, both (1) and (2) quickly turn sour, and are resolved into terchloracetic, carbonic, and hydrochloric acid:

$$C^6Cl^6O^4 + 4HO = C^4Cl^3H,O^4 + 3HCl + 2CO^2.$$

Similarly with aqueous fixed alkalis, they yield a terchloracetate and carbonate of the alkali, together with a metallic chloride:

$$C^6Cl^6O^4 + 6KO = C^4Cl^3K,O^4 + 3KCl + 2(KO,CO^2).$$

3. When either (1) or (2) is dropped into aqueous ammonia, each drop makes a hissing noise, like red-hot iron plunged into water, developes heat, and soon produces an abundant white precipitate, consisting of chloracetamide and sal-ammoniac, separable by ether which dissolves the former, or by water which takes up the latter; carbonate of ammonia is likewise formed. The first stage of the action probably consists in the formation of chloracetamide, sal-ammoniac, and phosgene:

$$C^6Cl^6O^4 + 2NH^3 = C^4NH^2Cl^3O^2 + NH^4Cl + 2CClO;$$

but the phosgene is converted by the excess of aqueous ammonia into of hydrochlorate and carbonate of ammonia:

$$2CClO + 4NH^3 + 2HO = 2NH^4Cl + 2(NH^3,CO^2).$$

4. Phosphuretted hydrogen gas passed through (2) forms chloracetyphide, with evolution of phosgene [and of hydrochloric acid]:

$$C^6Cl^6O^4 + PH^3 = C^4PH^2Cl^3O^2 + 2CClO + HCl.$$

5. Either (1) or (2) dropped into wood-spirit, disappears quickly, raising the temperature of the liquid nearly to the boiling point; and on the addition of water, two layers are formed, the upper, which is watery, containing hydrochloric acid, together with the excess of wood-spirit, while the lower, which is oily, is a mixture of chloromethylic formiate (VII, 309,) and terchloromethylic acetate. Perhaps in this manner:

$$C^6Cl^6O^4 + 2C^2H^4O^2 = C^4H^3ClO^4 + C^6H^3Cl^3O^4 + 2HCl.$$

With alcohol, (1) and (2) react in a precisely similar manner, excepting that in this case the oily mixture consists of chlorovinic formiate and terchlorovinic acetate, which may be separated by distillation, the former passing over at 100°, the latter between 160° and 165°:

$$C^6Cl^6O^4 + 2C^4H^6O^2 = C^6H^5ClO^4 + C^8H^5Cl^3O^4 + 2HCl.$$

The oily mixtures obtained with wood-spirit and with alcohol, differ from one another in this respect: that the product obtained with wood-spirit yields with ammonia, chloracetamide, and urethylane (VII, 291), while that obtained with alcohol yields chloracetamide and urethane (Cloez).

The corresponding compound of the methylene-series may be inserted in this place.

Perchloromethylic Formiate. $C^4Cl^4O^4 = C^2Cl^3O, C^2ClO^3$.

Cahours (1846). *Compt. rend.* 23, 1071. — *N. Ann. Chim. Phys.* 19, 252.

Perchlorameisenformester, Formiate de Methyle perchloré.

Perfectly anhydrous methylic formiate is placed in a bottle filled with dry chlorine gas, and exposed for some days to the sun (the action though violent at first soon diminishes in intensity), till after about 14 days, the colour of the chlorine no longer diminishes. The liquid, which is coloured by free chlorine, is then distilled, the portion which distils over below 190°, collected apart, and rectified several times, the more volatile portion being each time collected.

Transparent, colourless, very thin liquid, of sp. gr. 1·724 at 10°, boiling at 180° to 181°, and having a strong pungent odour, like that of phosgene.

When passed in the state of vapour through a tube heated to between 340° and 350°, it is converted almost wholly into phosgene gas, with which indeed it is metameric. — Aqueous ammonia acts violently upon it, forming white, nacreous chloracetamide (containing 14·61 p. c. C, 1·24 H, and 65·11 Cl, besides N and O), and sal-ammoniac. [It is impossible to express this decomposition by a simple equation, unless other products are present; if the nacreous matter is really chloracetamide, we have here an instance of the conversion of a conjugated compound of the methylene series into a compound of the ethylene series.] — Potash, even when hot and concentrated, exerts scarcely any decomposing action. Alcohol decomposes it, with formation of chlorovinic formiate; wood-spirit and fusel-oil form similar products (Cahours).

				Cahours.
4 C	24·0	12·15		12·31
4 Cl	141·6	71·66		71·69
4 O	32·0	16·19		15·95
H				0·05
$C^4Cl^4O^4$	197·6	100·00		100·00

Bichlorovinic Acetate. $C^6H^6Cl^2O^4 = C^4H^5O, C^4HCl^2O^3$.

Malaguti (1839). *Ann. Chim. Phys.* 70, 367; also *Ann. Pharm.* 32, 38; also *J. pr. Chem.* 18, 50.

Leblanc. *N. Ann. Chim. Phys.* 10, 197; abstr. *Compt. rend.* 17, 175; abstr. *J. pr. Chem.* 32, 80.

Bichloracetic Ether, Vinic Bichloracetate; Bichloressigvinester, Bichloressigäther, Ether acetique bichloruré.

Formation (VIII, 498). When acetic ether is introduced into a bottle filled with dry chlorine gas, in such proportion that each atom of the ether shall be in contact with more than 8 At. chlorine, and the action allowed to go on, first in the shade, afterwards in continually

stronger sunshine (sunshine from the beginning would cause an explosion attended with deposition of charcoal), the several chlorinated ethers, continually richer in chlorine, mentioned on page 498, vol. VIII, are successively produced. It is, however, not always possible to obtain the particular compound required, the compounds $C^8HCl^7O^4$ and $C^8Cl^8O^4$ being the only ones that can be produced with certainty. Other products are also formed, such as acetic acid, terchloracetic acid (which collects in crystals on the sides of the vessel), hydrochloric ether, sesquichloride of carbon, and certain oils, scarcely soluble in water. The less carefully the chlorine has been dried, the greater is the quantity of terchloracetic acid and other products soluble in water, formed (Leblanc). — When all moisture was excluded, Cloez obtained no sesquichloride of carbon.

Preparation. Dry chlorine gas is passed (in the shade, according to Leblanc) through acetic ether cooled from without, whereupon a large quantity of hydrochloric acid gas is evolved, especially in the latter part of the operation. As soon as the action of the chlorine has ceased, the more volatile portions of the resulting oily liquid are distilled off, till the residue begins to turn brown at about 110°; after which the colourless acid, and fuming liquid is quickly washed with water (if it stood longer, it would dissolve in the form of acetic and hydrochloric acid), and dried in vacuo over oil of vitriol and lime (Malaguti, Leblanc).

Properties. Transparent, colourless liquid of sp. gr. 1·301 at 12° (Malaguti); 1·30 at 15° (Leblanc). Smells something like acetic acid, tastes like pepper, and produces irritation in the throat (Malaguti).

				Malaguti.	Leblanc.
8 C	48·0	30·61		30·72	30·8
6 H	6·0	3·83		3·98	4·1
2 Cl	70·8	45·15		44·85	
4 O	32·0	20·41		20·45	
$C^8H^6Cl^2O^4$	156·8	100·00		100·00	

Decompositions. 1. Bichlorovinic acetate becomes coloured at 110°, and gives off hydrochloric acid (Malaguti). — 2. When subjected for some time to the action of chlorine in very bright sunshine, it is ultimately converted into $C^8Cl^8O^4$, part of which compound is by the further action of the clorine transformed into C^4Cl^6 (Leblanc). When left for several days under water, it dissolves completely in the form of acetic and hydrochloric acid (Malaguti):

$$C^8H^6Cl^2O^4 + 4HO = 2C^4H^4O^4 + 2HCl.$$

4. It is not immediately decomposed by aqueous potash, but alcoholic potash decomposes it instantly, forming acetate of potash and chloride of potassium (Malaguti, Leblanc):

$$C^8H^6Cl^2O^4 + 4KO = 2C^4H^3KO^4 + 2KCl.$$

purified in the same manner as Malaguti purifies his bichloracetic ether, a compound ether is obtained which smells and tastes like bichloracetic ether, and consists of $C^8H^5Cl^3O^4$ (see the above analysis), but is not decomposed by aqueous potash into alcohol and terchloracetate of potash, but yields with that reagent, chloride of potassium, chlorinated, deliquescent potash-salts, and a sweet, oily liquid no longer decomposible by potash (Leblanc). [Can this ether be $C^4Cl^3H^2O,C^4H^3O^3$?]

Quadrichlorovinic Acetate. $C^8H^4Cl^4O^4=C^4ClH^4O,C^4Cl^3O^3$.

Fel. Leblanc (1844). *N. Ann. Chim. Phys.* 10, 212.

Bichloracetic ether is exposed to the autumn sun in bottles filled with dry chlorine gas, and the product purified in the ordinary way.

Oil of sp. gr. 1·485 at 25°.

Decomposed by potash-ley into a chlorinated oil, chloride of potassium, terchloracetate, and other chloracetates of potash (Leblanc).

			Leblanc.
8 C	48·0	21·28	21·60
4 H	4·0	1·77	2·02
4 Cl	141·6	62·76	63·09
4 O	32·0	14·19	13·29
$C^8H^4Cl^4O^4$	225·6	100·00	100·00

Quintichlorovinic Acetate. $C^8H^3Cl^5O^4=C^4Cl^2H^3O,C^4Cl^3O^3$.

Fel. Leblanc. *N. Ann. Chim. Phys.* 10, 212.

Produced, like the preceding compound, if the liquid be heated at the same time, but in such a manner that the gas above it may be protected from the action of the solar rays.

With strong potash it forms the same decomposition-products as the preceding compound, yielding however a larger quantity of terchloracetate of potash (Leblanc).

			Leblanc.
8 C	48	18·46	18·80
3 H	3	1·15	1·35
5 Cl	177	68·08	67·40
4 O	32	12·31	12·45
$C^8H^3Cl^5O^4$	260	100·00	100·00

Sextichlorovinic Acetate. $C^8H^2Cl^6O^4=C^4H^2Cl^2O,C^4Cl^3O^3$.

Leblanc. *N. Ann. Chim. Phys.* 10, 212.

Formed when the preceding compound is exposed for two days to the sun in a bottle filled with chlorine.

Oily liquid of sp. gr. 1·698 at 23·5° (Leblanc).

				Leblanc.
8 C	48·0	16·31		16·1
2 H	2·0	0·68		1·0
6 Cl	212·4	72·14		73·0
4 O	32·0	10·87		9·9
$C^8H^2Cl^6O^4$	294·4	100·00		100·0

Septichlorovinic Acetate. $C^8HCl^7O^4 = C^4HCl^4O, C^4Cl^3O^3$.

Fel. Leblanc (1843). *N. Ann. Chim. Phys.* 10, 206.

Formation and Preparation. Dry chlorine gas is passed for some time through terchloracetic ether, by daylight and at a temperature gradually rising to 100°.

Oily liquid of sp. gr. 1·692 at 24·5°.

			Leblanc.	
			oily.	*crystalline.*
8 C	48·0	14·60	14·7	14·70
H	1·0	0·30	0·4	0·49
7 Cl	247·8	75·37	74·5	74·70
4 O	32·0	9·73	10·4	10·11
$C^8HCl^7O^4$	328·8	100·00	100·0	100·00

Dry chlorine gas passed for a long time through this ether at 110° converts it into perchlorovinic aectate.

It is insoluble in water (Leblanc).

Crystalline modification of Septichlorovinic Acetate.

Preparation. When bichloracetic ether is introduced into bottles filled with dry chlorine gas, and exposed to sunshine for some months in winter, a mixture of oil and crystals is formed. The bottles are rinsed with water; the insoluble portion treated with a quantity of vinic ether just sufficient to dissolve the crystals, whereby two layers of liquid are obtained, the lower being an ethereal solution, and the upper an oil; these two liquids are separated by a pipette; the ethereal solution left to evaporate; and the resulting crystals, still contaminated with oil, dried upon blotting paper.

The crystals thus obtained are rather soft; they melt at 100°, and appear to be incapable of volatilizing without decomposition. They have the composition above given. — They are insoluble in water, sparingly soluble in cold alcohol of ordinary strength, but dissolve very readily in ether (Leblanc).

Leblanc did not succeed more than once in obtaining these crystals.

Perchlorovinic Acetate. $C^8Cl^8O^4 = C^4Cl^3O,C^4Cl^5O^3$?

FELIX LEBLANC. *N. Ann. Chim. Phys.* 10, 200; abstr. *Compt. rend.* 17, 1175; abstr. *J. pr. Chem.* 32, 80. — *Compt. rend.* 21, 925.

MALAGUTI. *Compt. rend.* 21, 445. — *N. Ann. Chim. Phys.* 16, 57; also *J. pr. Chem.* 37, 432.

CLOEZ. *N. Ann. Chim. Phys.* 17, 304; abstr. *Compt. rend.* 21, 874; abstr. *N. J. Pharm.* 9, 15; abstr. *J. pr. Chem.* 37, 343.

Perchlorsseigvinester, Perchloressigäther, Ether acetique perchloré, Ether perchloracetique. — Discovered by Leblanc in 1843.

Formation and Preparation. 1. To replace all the hydrogen in bi- or terchlorovinic acetate by chlorine, requires the brightest summer sunshine and a heat of at least 110°, and even then the substitution is very slow. One of the two ethers just mentioned is introduced into a tubulated retort having its lower part immersed in a concentrated chloride of calcium bath heated ultimately to 110°, and its upper part exposed to the sun. The passage of the dry chlorine must be continued for at least 100 hours to convert the bichlorovinic acetate into septichlorovinic acetate, and the conversion of the latter into perchlorovinic acetate takes place only in the brightest summer sunshine, and very slowly even then. Even before the transformation is complete, crystals of sesquichloride of carbon sublime, proceeding from the further decomposition of perchloracetic ether by chlorine; but the passage of the chlorine must be still continued till a sample of the liquid when analyzed is no longer found to contain hydrogen. Dry carbonic acid gas is then passed through the liquid to free it from absorbed chlorine and hydrochloric acid gas; the perchloracetic ether quickly precipitated therefrom by water, and quickly washed with water to remove the dissolved terchloracetic acid proceeding from moisture in the chlorine gas. The ether is then separated from the water with a pipette; heated for a few minutes to 100°, whereby it loses its turbidity; then drawn off clear with the pipette; dried in vacuo over oil of vitriol and hydrate of potash; and heated in a retort till the boiling point rises to about 200°, and nearly all the dissolved sesquichloride of carbon is thereby volatilized. The residue in the retort quickly washed with water and dried in vacuo as above, yields pure perchlorovinic acetate (Leblanc).

2. Perfectly dry chlorine gas is passed, first by diffused daylight, afterwards in sunshine, through perfectly pure and dry acetic ether contained in a tubulated retort; the liquid then introduced into large bottles filled with dry chlorine, and exposed to the sun (whereby no sesquichloride of carbon is formed); a large quantity of dry carbonic acid gas passed through it to remove free chlorine, &c.; and the liquid finally distilled in a retort filled with carbonic acid, till the residue becomes coloured (Cloez). By this distillation, however, as afterwards shown by Malaguti, part of the perchlorovinic acetate is converted into the isomeric compound, chloraldehyde.

Properties. Colourless oil, which remains liquid at a few degrees below 0°; sp. gr. 1·79 at 25°; boils at 245°, but is partly decomposed thereby (*vid. inf.*). Has a strong penetrating odour like that of chloral,

and a burning taste. When recently prepared and quite dry, it does not redden litmus, or produce an immediate precipitate in a silver-solution; but after a few minutes, the precipitate appears (Leblanc).

			Leblanc.	
			a.	*b.*
8 C	48·0	13·22	13·3	13·48
H			0·2	0·03
8 Cl	283·2	77·97	77·1	77·57
4 O	32·0	8·81	9·4	8·92
$C^8Cl^8O^4$	363·2	100·00	100·0	100·00

a was prepared from bichloracetic ether, *b* from terchloracetic ether.

Decompositions. 1. When the vapour of perchloracetic ether is passed through a glass tube filled with fragments of glass and heated to 400°, a fuming mixture of undecomposed perchloracetic ether and chloraldehyde is obtained, the quantity of the latter increasing at each repetition of the process (Malaguti):

$$C^8Cl^8O^4 = 2C^4Cl^4O^2.$$

This transformation was previously suspected by Leblanc, on finding that the vapour-density of the ether determined at 311°, amounted to only 9·9, instead of 12·5 which is its calculated value. Part of the ether is, in fact, converted into chloraldehyde, even by distillation. If the ether prepared by (2), which has therefore been already once distilled (and therefore already contains chloraldehyde) be distilled a second time, the boiling point rises from 105° to 280°, and the more volatile portion, which first passes over, consists chiefly of chloraldehyde (Cloez). — 2. Chlorine gas passed through perchloracetic ether heated to 120° and exposed to the sun, produces a large quantity of sesquichloride of carbon which sublimes. Hence the chlorine takes the place of oxygen (Leblanc):

$$C^8Cl^8O^4 + 4Cl = 2C^4Cl^6 + 4O.$$

[The evolution of oxygen remains to be proved]. — 3. Perchloracetic ether is gradually decomposed in contact with water, and therefore also in moist air, into terchloracetic and hydrochloric acid (Leblanc):

$$C^8Cl^8O^4 + 4HO = 2C^4Cl^3HO^4 + 2HCl.$$

4. Strong potash-solution decomposes it almost instantly and in a similar manner (Leblanc):

$$C^8Cl^8O^4 + 4KO = 2C^4Cl^3KO^4 + 2KCl.$$

5. It absorbs ammoniacal gas, and immediately solidifies to a mixture of chloracetamide and sal-ammoniac. When it is dropped into aqueous ammonia, each drop hisses like red-hot iron falling into water, evolving also a white fume, and forming chloracetamide which precipitates, and sal-ammoniac which remains in solution (Malaguti, Cloez):

$$C^8Cl^8O^4 + 4NH^3 = 2C^4NH^2Cl^3O^2 + 2NH^4Cl.$$

6. Alcohol decomposes perchloracetic ether, with evolution of heat, forming terchloracetic ether and hydrochloric acid (Malaguti):

$$C^8Cl^8O^4 + 2C^4H^6O^2 = 2C^8H^5Cl^3O^4 + 2HCl.$$

In the reactions 4, 5, and 6, perchloracetic ether agrees exactly with chloraldehyde (Malaguti).

Oil of vitriol neither dissolves this ether nor colours it (Leblanc).

Perchlorovinic Oxalate. $C^{12}Cl^{10}O^8 = 2C^4Cl^5O,C^4O^6$.

MALAGUTI. *Ann. Chim. Phys.* 74, 299; also *Ann. Pharm.* 37, 66; also *J. pr. Chem.* 22, 199. — *N. Ann. Chim. Phys.* 16, 46; abstr. *J. pr. Chem.* 37, 430.

Perchloroxalic ether, Perchloroxalvinester, Chloroxaläther, Ether chloroxalique. — Discovered by Malaguti in 1840.

Formation and Preparation. Chlorine acts upon oxalic ether only when aided by heat and light. To obtain perchloroxalic ether, dry chlorine gas is passed through oxalic ether contained in a tubulated retort which is heated in the water-bath, and at the same time exposed to the sun. After an hour or two, hydrochloric acid gas begins to escape, and continues during the rest of the process. In 25 to 30 hours, the liquid becomes syrupy, and deposits crystals of perchloroxalic ether, from which the supernatant liquid must be decanted as often as they collect in sufficient quantity to interrupt the passage of the gas; the process must be continued till the liquid is almost wholly converted into crystals. The whole mass of crystals is then pressed between blotting paper till they no longer make the paper greasy; the mass pulverized, washed on a filter of Swedish blotting paper with acetic ether, till the liquid which runs through no longer reddens litmus or but very slightly; the residue again pressed between paper; again washed, &c., till the crystals no longer taste sour. To free them from the paper-fibres which get mixed with them during these several processes, 0·3 or 0·4 grm. of the crystals is spread out on the inner surface of a platinum crucible having a diameter of 6 centim.; the crucible placed upon a metal plate; and carefully heated by a spirit-lamp quickly moved about under the plate, so that the ether may melt and run down to the bottom, while the paper-fibres remain sticking to the sides. The ether solidifies to a crystalline crust, which for further purification is placed in water for 48 hours, then washed, and quickly dried in vacuo over oil of vitriol. The quantity of the ether fused in one operation must not be greater than that above stated; otherwise the paper-fibres are apt to char and impart to the ether a sour and disagreeable odour, so that it will require to be washed and pressed again. Even with 0·3 grm. a certain amount of decomposition takes place; but the layer of melted liquid being very thin, the greater part of the decomposition-products escape in the form of a dense suffocating vapour.

Properties. Colourless, four-sided tables, transparent when recently prepared, but opaque after being kept for some time. Melts at 144° with incipient decomposition. Inodorous, tasteless, perfectly neutral.

				Malaguti.
12 C	72	14·69		14·82
H				0·10
10 Cl	354	72·25		70·90
8 O	32	13·06		14·18
$C^{12}Cl^{10}O^8$	490	100·00		100·00

Decompositions. 1. Perchloroxalic ether heated in a distillatory apparatus, is resolved between 280° and 290° into a mixture of carbonic

oxide and phosgene gas—the phosgene predominating at first, and the carbonic oxide afterwards—and a transparent, colourless distillate, consisting of chloraldehyde and undecomposed perchloroxalic ether, which, after several repetitions of the distillation, is at length completely resolved into the gaseous mixture and chloraldehyde. The ether undergoes the same decomposition at ordinary temperatures, when kept for some time even in a sealed glass tube; it then becomes fuming, and acquires the odour of phosgene:

$$C^{12}Cl^{10}O^8 = 2C^4Cl^4O^2 + 2CClO + 2CO.$$

2. Perchloroxalic ether exposed to damp air, becomes sour, fuming, and deliquescent. — 3. When boiled with potash-ley, it dissolves, gives off a sweet-smelling vapour and a small quantity of chloroform, and leaves a residue of oxalate, terchloracetate, and formiate of potash, together with chloride of potassium. The products first formed are oxalate of potash, terchloracetate of potash, and chloride of potassium:

$$C^{12}Cl^{10}O^8 + 8KO = C^4K^2O^8 + 2C^4Cl^3KO^4 + 4KCl.$$

But the excess of potash decomposes part of the terchloracetate, yielding chloroform and carbonate of potash:

$$C^4Cl^3KO^4 + HO + KO = C^2HCl^3 + 2(KO,CO^2);$$

and afterwards part of the chloroform, yielding formiate of potash and chloride of potassium:

$$C^2HCl^3 + 4KO = C^2HKO^4 + 3KCl.$$

4. With ammonia, perchloroxalic ether forms sal-ammoniac, chloroxethamide, another amidogen compound, and one or two peculiar ammoniacal salts. Dry ammoniacal gas passed over the pulverized ether is absorbed, with evolution of heat, and formation of a white fume, a white fibrous and laminated sublimate, a yellowish crystalline crust, and a disagreeably smelling vapour. When the mass thus produced is treated with common ether, sal-ammoniac remains behind; the ethereal solution yields by evaporation crystals of chloroxethamide; the mother-liquor, when further evaporated, deposits flat grains of another amide; and the mother-liquor decanted from this, leaves, when evaporated in vacuo, a tolerably copious residue, which, under the microscope, presents the appearance of a mixture of grains, prisms, four-sided tables, and amorphous matter. This residue gives off ammonia when treated with potash-hydrate, a result which cannot be due to the presence of oxalate or formiate of ammonia, inasmuch as the residue is completely soluble in ether, and its aqueous solution gives no perceptible turbidity with chloride of calcium or nitrate of silver. — With aqueous ammonia, in which every drop of the ether makes a loud hissing noise, the same products are formed, excepting that the quantity of chloroxethamide produced is much less, and that a little oxamide is formed which falls down together with the chloroxethamide as a white powder.

5. With alcohol, perchloroxalic ether becomes heated, gives off a small quantity of carbonic oxide gas, often mixed with carbonic acid gas and vapour of hydrochloric ether, and forms a pale yellow liquid, which, on the addition of water, deposits a pale yellow, oily mixture of chloroxethide = $C^5Cl^5O^7$, and a small quantity of oxalic ether, while chloroxalovinic, terchloracetic, oxalic and hydrochloric acid remain in solution. — The products vary according to the temperature, strength,

and quantity of the alcohol. In the following equation, Malaguti supposes that all the above-named acids form compound ethers with the alcohol, and overlooks the carbonic oxide, carbonic acid, and the chloroxalovinic acid found in the aqueous solution:

$$3C^{12}Cl^{10}O^8 + 14C^4H^6O^2 = \underbrace{8C^4H^5Cl}_{\text{hydrochloric ether.}} + \underbrace{C^{12}H^{10}O^8}_{\text{oxalic ether.}} + \underbrace{4C^8H^5Cl^3O^4}_{\text{terchloracetic ether.}} + \underbrace{2C^8Cl^5O^7}_{\text{chloroxethide.}} + 14HO.$$

6. Chloroxalovinic ether is likewise immediately decomposed by wood-spirit, acetone, fusel-oil and oil of turpentine, more slowly by vinic ether and acetic ether, and very slowly by acetate of methyl (Malaguti).

When wood-spirit is added drop by drop to perchloroxalic ether, as long as it causes any rise of temperature and evolution of hydrochloric acid gas, and water added after cooling, an oily mixture of chloromethylic formiate and methylic oxalate falls to the bottom. (Cahours, *N. Ann. Chim. Phys.* 19, 342; also *J. pr. Chem.* 40, 429.)

Chloroxethide. $C^8Cl^5O^7 = C^4Cl^5O,C^4O^6$?

MALAGUTI (1840). *Ann. Chim. Phys.* 74, 308; also *J. pr. Chem.* 22, 208.

Chloroxäthid, Acide chloroxalovinique anhydre, Chloroxétide.

When perchloroxalic ether is added to alcohol, and water added to the mixture, chloroxethide, contaminated with a small quantity of oxalic ether, is precipitated in the form of a pale yellow oil. This oil has a sp. gr. of 1·3485 at 16·5°; a vinous odour; persistent sweet taste, with bitter after-taste; and does not redden litmus, excepting after exposure to moist air.

It is insoluble in water, which however becomes acid by contact with it, but without taking up hydrochloric or oxalic acid. It dissolves in cold aqueous fixed alkalis, forming a chloroxalovinate of the alkali; but at a boiling heat it forms an alkaline oxalate and a metallic chloride:

$$C^8Cl^5O^7 + KO = C^4Cl^5KO^2,C^4O^6;$$

and

$$C^8Cl^5O^7 + 9KO = 2C^4K^2O^8 + 5KCl.$$

With ammoniacal gas or aqueous ammonia it immediately forms pure crystalline chloroxethamide:

$$C^8Cl^5O^7 + NH^3 = C^8NH^2Cl^5O^6 + HO.$$

It mixes in all proportions with alcohol and vinic ether (Malaguti).

				Malaguti.
8 C	48·0	17·08		17·06
5 Cl	177·0	62·99		62·59
7 O	56·0	19·93		20·35
$C^8Cl^5O^7$	281·0	100·00		100·00

Chloroxalovinic Acid. $C^8HCl^5O^5 = C^4Cl^5HO^2, C^4O^6$.

MALAGUTI (1840). *Ann. Chim. Phys.* 74, 308; also *J. pr. Chem.* 22, 208.

Chlorweinoxalsäure, Chloroxaloweinsäure, Acide chloroxalvinique, Acide chloroxétique.

Formation. 1. In the decomposition of perchloroxalic ether by alcohol (p. 243). — 2. When chloroxethide is treated with cold aqueous solution of fixed alkalis. — 3. When chloroxethamide is treated with aqueous ammonia:

$$C^8NH^2Cl^5O^6 + 2HO = NH^3, C^8HCl^5O^8.$$

Preparation. By placing chloroxethamide in contact with aqueous ammonia till it is completely dissolved, and evaporating in vacuo, crystallized chloroxalovinate of ammonia is obtained. This salt is dissolved in water; the solution mixed with carbonate of soda and evaporated, first in the sand-bath, afterwards in vacuo over oil of vitriol; the chloroxalovinate of soda extracted from the residue by absolute alcohol; the soda precipitated from this solution by the exact quantity of sulphuric acid required; the liquid filtered; any excess of sulphuric acid that it may contain, precipitated by baryta-water; the liquid filtered again; and the alcoholic solution of chloroxalovinic acid evaporated to the crystallizing point, first over the water-bath, and then in vacuo.

Properties. Colourless needles, which melt at a gentle heat. Has a burning taste, and forms a white spot on the tongue; if placed for a while on the back of the hand, it produces violent pain and a white spot surrounded with an inflamed ring.

				Malaguti.
8 C	48	16·55		16·26
H	1	0·35		
5 Cl	177	61·03		60·20
8 O	64	22·07		
$C^8HCl^5O^8$	290	100·00		

Oxalovinic acid in which 5H are replaced by 5Cl.

Combinations. The acid dissolves in all proportions in water and deliquesces very quickly in the air.

Chloroxalovinate of Ammonia. — Preparation (*vid. sup.*). Crystalline; may be fused without decomposing; tastes very bitter and pungent; has a faint acid reaction. When heated to the boiling point, it decomposes, without evolving ammonia, and gives off thick vapours smelling of acetic acid. Deliquesces and turns yellowish in the air, but becomes white again when dried in vacuo. Soluble in alcohol.

			Malaguti.
8 C	48	15·63	15·68
N	14	4·56	4·42
4 H	4	1·30	1·39
5 Cl	177	57·66	57·44
8 O	64	20·85	21·07
NH^4O,C^4Cl^5O,C^4O^6	307	100·00	100·00

The acid dissolves in all proportions in vinic ether and in alcohol (Malaguti).

f. Amidogen Nuclei.

Amidogen-nucleus C^4AdH^3.

Acetamide. $C^4NH^5O^2=C^4AdH^3,O^2$.

Dumas, Malaguti & Leblanc. (1847.) *Compt. rend.* 25, 657.

Produced abundantly by the action of aqueous ammonia upon acetic ether:

$$C^8H^8O^4 + NH^3 = C^4NH^5O^2 + C^4H^6O^2.$$

White, crystalline; melts at 78°, and solidifies on cooling in beautiful crystals; boils at 121°, forming a diatomic vapour.

Anhydrous phosphoric acid readily converts it into water and cyanate of methyl:

$$C^4NH^5O^2 = C^2H^3,C^2N + 2HO.$$

When mixed with potassium, it gives off hydrogen and carburetted hydrogen gas, without forming $C^2H^3KO^2$, and leaves potash mixed with cyanide of potassium (Dumas, Malaguti, Leblanc).

¶ Ethylacetamide. $C^6NH^7O^2=C^4Ad\{^{H^2}_{Ae}\}O^2=N\left\{\begin{matrix}C^4H^5\\C^4H^3O^2\\H\end{matrix}\right.$.

Wurtz. *N. Ann. Chim. Phys.* 30, 491; further: *Compt. rend.* 36, 180; *Chem. Soc. Qu. J.* VII. 91.

Formation and Preparation. 1. Obtained by the action of ethylamine on acetic ether:

$$C^8H^8O^4 + C^4H^7N = C^6NH^7O^2 + C^4H^6O^2.$$

Acetic ether dissolves readily in aqueous ethylamine. The solution evaporated first over the water-bath, and then in vacuo over oil of vitriol, gradually condenses to a syrupy liquid which refuses to crystallize. — 2. By the action of cyanic ether on glacial acetic acid, carbonic acid being evolved at the same time:

$$C^4H^4O^4 + C^6NH^5O^2 = C^6NH^7O^2 + 2CO^2.$$

or

$$\left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}O^2 + \left.\begin{matrix}C^2N\\C^4H^5\end{matrix}\right\}O^2 = N\left\{\begin{matrix}C^4H^5\\C^4H^3O^2\\H\end{matrix}\right. + 2CO^2.$$

Properties. Differs from acetamide in being liquid, but less volatile. Boils at about 200°, and distils, almost without decomposition. Caustic potash decomposes it, yielding ethylamine and acetate of potash:

$$C^8NH^9O^2 + 2KO = C^4H^7N + C^4H^2K^2O^4.$$

Anhydrous phosphoric acid decomposes it with separation of carbon (Wurtz).

¶ Ethylodiacetamide.

$$C^{12}NH^{11}O^4 = O^2 = C^4Ad\left\{\begin{matrix} H \\ C^4H^5 \\ C^4H^3O^2 \end{matrix}\right\}O^2 = N\left\{\begin{matrix} C^4H^5 \\ C^4H^3O^2 \\ C^4H^3O^2 \end{matrix}\right.$$

Wurtz. *Compt. rend.* 36, 180.

Formed by the action of cyanic ether on anhydrous acetic acid:

$$\left.\begin{matrix} C^4H^3O^2 \\ C^4H^3O^2 \end{matrix}\right\}O^2 + C^4H^5,C^2NO^2 = N\left\{\begin{matrix} C^4H^5 \\ C^4H^3O^2 \\ C^4H^3O^2 \end{matrix}\right. + 2CO^2.$$

When the two liquids, in about equal volumes, are enclosed in a tube of green glass, the tube hermetically sealed and heated in the oil-bath to 180°, the reaction takes place as above, carbonic acid being set free.

The formation and constitution of this and the two preceding compounds agree but ill with the nucleus-theory. The supposition that acetamide contains 1 At. amidogen and 3 At. hydrogen, and that in ethylacetamide one of the three H-atoms is replaced by ethyl, and in ethylo-diacetamide, one is replaced by ethyl and a second by acetyl, is scarcely tenable. The theory which agrees best with their mode of formation is that acetamide is ammonia in which 1 At. H is replaced by the radical $C^4H^3O^2$ (othyl or acetyl) $= N\left\{\begin{matrix} H \\ H \\ C^4H^3O^2 \end{matrix}\right.$; ethylacetamide is ammonia in which 1 At. H is replaced by acetyl and another by ethyl; and ethylo-diacetamide, is ammonia in which 2 At H are replaced by acetyl and the third by ethyl. This view of their constitution assimilates them to the compound ammonias, ethylamine, methylethylamine, &c. It is true that they do not exhibit basic reactions; but then it must be remembered that they contain the chlorous radical $C^4H^3O^2$. ¶

Glycocol. $C^4NH^5O^4 = C^4AdH^3,O^4$.

Braconnot. *Ann. Chim. Phys.* 13, 114; also *Schw.* 29, 344; also *Gilb.* 70, 390.

Boussingault. *Compt. rend.* 7, 493; also *J. pr. Chem.* 15, 453; also *Ann. Pharm.* 28, 80. — *N. Ann. Chim. Phys.* 1, 257; also *Ann. Pharm.* 39, 304; also *J. pr. Chem.* 24, 173.

Mulder. *J. pr. Chem.* 16, 290; abstr. *Ann. Pharm.* 28, 79. — *J. pr. Chem.* 38, 294.

Dessaignes. *Compt. rend.* 21, 1224; also *N. Ann. Chim. Phys.* 17, 50; also *J. pr. Chem.* 37, 244; also *Ann. Pharm.* 58, 322.

Laurent. *Compt. rend.* 22, 789.

E. N. Horsford. *Ann. Pharm.* 60, 1.

Gerhardt. *N. J. Pharm.* 11, 154.

Leimsüss, Leimzucker, Glykokoll, Sucre de Gélatine.

Occurs as a copula in hippuric acid (Dessaignes); and in cholic acid (Strecker).

Formation. By the action of sulphuric acid on gelatin (Braconnot); or of potash on gelatin or meat (Mulder).

Preparation. 1. A mixture of 1 pt. pounded glue, and 2 pts. oil of vitriol, is set aside for 24 hours, then diluted with 8 pts. of water; the liquid kept boiling for 5 hours, the water being renewed as it evaporates; neutralized with chalk after further dilution; and the filtrate evaporated to a syrup. This syrupy liquid when left to itself for some time, yields crystals, which are washed with weak spirit, pressed between linen, and purified by crystallization from water (Braconnot). — These crystals are still contaminated with soluble salts, and therefore yield from 2 to 11 p.c. of ash. They must therefore be boiled for some time with milk of baryta, which does not cause any evolution of ammonia; the baryta precipitated from the filtrate by careful addition of sulphuric acid; and the liquid filtered and evaporated to the crystallizing point, which is very soon attained (Boussingault). — Mulder obtained, by Braconnot's process, very little glycocol, but a large quantity of leucin.

2. Glue is boiled with potash-ley, which causes a copious evolution of ammonia; the liquid neutralized with sulphuric acid; evaporated; separated from the sulphate of potash, which crystallizes out; again evaporated; and the residue exhausted with alcohol, which takes up the glycocol, together with a small quantity of leucin. As leucin dissolves in alcohol much more readily than glycocol, the two substances are easily separated —The purification is easier in this process than in (1) because no leucin is formed (according to Mulder, a small quantity); the glycocol thus obtained also leaves a small quantity of ash: milk of lime may be used instead of potash-ley (Boussingault).

3. Four ounces of hippuric acid (prepared by Bensch's process), is heated in a flask, of 1 litre capacity, with 16 oz. of strong hydrochloric acid till it dissolves; the heat then continued half an hour longer; the liquor diluted with water, which throws down heavy oily drops of fused benzoic acid; filtered, when sufficiently cooled, to separate the benzoic acid, which has then for the most part crystallized out; the benzoic acid washed with water as long as the water thereby acquires a sour taste; the filtrate containing hydrochlorate of glycocol, together with hydrochloric and benzoic acid, evaporated nearly to dryness in an open basin on the water-bath, to expel the free acids; water then added; the solution again evaporated; and these operations repeated till the residue consists of pure hydrochlorate of glycocol. This salt mixed with aqueous ammonia sufficient to produce an alkaline reaction, then mixed with absolute alcohol, and set aside for some time, deposits nearly all the glycocol as a crystalline powder, while sal-ammoniac, together with a trace of benzoic acid, remains in solution. The crystalline powder is washed on the filter with absolute alcohol, till the liquid which runs off no longer produces turbidity in a silver-solution (Horsford).

4. Glycocol is likewise obtained by boiling cholic acid with hydrochloric acid or aqueous alkalis (Strecker).

Properties. Crystallizes more readily than common sugar, in hard, colourless, aggregated tables, which crackle between the teeth (Braconnot). Large prisms and rhombohedrons (Mulder). The saturated

solution in water or weak spirit yields by spontaneous evaporation, crystals of the oblique prismatic system (Horsford). Melts more easily than common sugar. About as sweet as grape-sugar (Braconnot); inodorous and very sweet (Mulder); less sweet than common sugar (Horsford); slightly sweet and leaves an unpleasant after-taste. (Boussingault). Neutral to vegetable colours (Mulder, Horsford). ¶ Perfectly pure glycocol, free from hydrochloric acid, reddens litmus-paper distinctly (Dessaignes, *Ann. Pharm.* 82, 237). ¶ — Permanent in the air (Mulder). When heated with strong potash, it exhibits a magnificent fire-red colour, which disappears on continuing the heat. Even in small quantity, it prevents the precipitation of aqueous sulphate of copper by potash, a blue mixture being in fact produced; a boiling aqueous solution of glycocol also dissolves oxide of copper, forming a blue solution, and yields needles on cooling (Horsford).

		Boussingault.	Mulder.		Laurent.	Horsford.
	Crystallized.	at 120°.	*earlier.*	*later.*		
4 C	24 .... 32·00	.... 33·85	.... 34·18	.... 32·11	.... 32·10	.... 31·98
N	14 .... 18·67	.... 20·00	.... 19·84	.... 18·73	.... 18·95	.... 18·79
5 H	5 .... 6·67	.... 6·44	.... 6·49	.... 6·85	.... 6·66	.... 6·87
4 O	32 .... 42·66	.... 39·71	.... 39·49	.... 42·31	.... 42·29	.... 42·36
$C^4NH^5O^4$	75 .... 100·00	.... 100·00	.... 100·00	.... 100·00	.... 100·00	.... 100·00

Mulder supposes that the first sample of glycocol which he analyzed and from which he deduced the formula $C^8N^2H^9O^7$, was contaminated with leucin; the same was perhaps the case with Boussingault's glycocol, which gave the formula $C^{12}N^4H^{18}O^{14}$. Gerhardt (*Précis*, 2, 442) first suggested the formula $C^4NH^5O^4$, which was soon afterwards confirmed by the investigations of Dessaignes upon hippuric acid, and subsequently by the analyses of Laurent, Mulder and Horsford. Mulder however doubles the formula, making it $C^8N^2H^{10}O^8$. Horsford likewise distinguishes a hypothetical anhydrous glycocol = $C^4NH^4O^3$, which with HO forms crystallized glycocol. According to the radical theory, this supposition is so far well founded that 1 At. H. in glycocol is replaceable by 1 At. of a metal.

The rational formula C^4AdH^3,O^4 is improbable for this reason: that glycocol gives off ammonia only when boiled with very strong alkalis, and that, if it contains 4O outside the nucleus, it should possess more decided acid properties. On the other hand, its acid nature is in accordance with the fact that it is capable of combining with metallic oxides, the reaction being attended with formation of 1 At. water; and that in combination with 1 At. of another acid, it forms a conjugated acid which according to Gerhardt's law (p. 222) saturates 1 At. of a base. According to this view, glycocol is acetic acid $C^4H^4O^4$ in which 1 At. H is replaced by 1 Ad. — Gerhardt accordingly regards glycocol as the amide of a bibasic acid $= C^4H^4O^6$:

$$C^4H^4O^6 + NH^3 = C^4H^5NO^4 + 2HO;$$

just as oxamic acid is produced from oxalic acid:

$$C^4H^2O^8 + NH^3 = C^4NH^3O^6 + 2HO.$$

Decompositions. 1. The crystals freed from adhering moisture by drying in vacuo at ordinary temperatures, do not undergo any further diminution in weight at 130° (Boussingault), or even at 150° (Horsford). By dry distillation they yield an ammoniacal distillate and a small quantity of white sublimate (Braconnot). At 178° they begin to melt, then

decompose, with formation of products having an empyreumatic animal odour, and leave a mass of tumefied charcoal (Mulder). — At 170°, the crystals turn brown at the lower part and give off gas, whilst the upper part melts and crystallizes again on cooling; at 190°, partial carbonization takes place (Horsford). — 2. When an aqueous solution of glycocol is separated from water by a piece of bladder, one polar wire [which?] of a 4-pair Bunsen's battery dipped into the solution, and the other into the water, gas is evolved at both poles, the liquid round the negative pole acquires an alkaline reaction, and that around the positive pole an acid reaction, perhaps from formation of ammonia and fumaric acid [or more probably maleic acid.] (Horsford).

3. In a stream of chlorine gas, the crystals immediately give off water and hydrochloric acid, and are converted into a brown resin partially soluble in water. The brown, strongly acid solution, deposits when filtered large crystals which have not been further examined. — The same decomposition is produced by bromine and by iodine (Mulder). — The saturated aqueous solution of glycocol rapidly absorbs chlorine gas, with formation of carbonic acid, and after three days' passage of the gas, is converted into a syrup containing a peculiar acid; but even after the gas has been passed through it for a week, a portion of the glycocol still remains undecomposed (Horsford).

To obtain the baryta-salt of this *peculiar acid*, the syrup is diluted with a small quantity of water; neutralized with ammonia; precipitated by chloride of barium; and the precipitate washed a little with water and dried, whereby its solubility in water is greatly diminished. The salt thus obtained is free from nitrogen, and contains 51·65 p.c. BaO, 13·08C, 1·98H, and 33·38O; it is therefore $BaO,C^3H^3O^6$.

4. Nitric acid boiled for some time with glycocol converts it into the peculiar acid above mentioned, just as chlorine does. So likewise does hydrochloric acid, when it is boiled for a long time with glycocol and chlorate of potash added frequently in small quantities. The same acid is also produced by the action of permanganate of potash (Horsford).

5. Oil of vitriol blackens glycocol when heated with it (Mulder). — When a solution of glycocol in dilute sulphuric acid is evaporated to a syrup, the residue dissolved in water, the liquid again evaporated, &c. &c., the evaporated mass ultimately solidifies in rhombic prisms, which are permanent in the air; have a sour taste, and give off ammonia with potash after being washed with alcohol and pulverized; their solution precipitates chloride of barium and bichloride of platinum. — These crystals contain 12·87 p.c. C, 14·51 N, 5·42 H, 25·35 O and 41·85 SO^3; they are therefore $= C^4N^2H^{10}O^6,2SO^3 = NH^4O,SO^3,HO + C^4NH^5O^4,SO^3$, *i.e.* sulphate of ammonia combined with sulphate of glycocol. Hence 1 At. glycocol probably yields 1 At. ammonia, which goes to form the double salt, while fumaric [maleic] acid is at the same time set free. — When glycocol is heated for several hours with dilute sulphuric acid, the water being replaced as it evaporates, the greater part of the sulphuric acid then precipitated by oxide of lead, and the rest by baryta-water, — the filtrate concentrated, first by evaporation, then over oil of vitriol, yields beautiful rhombohedrons, which are sparingly soluble in cold water; insoluble in alcohol and ether; give off ammonia when treated with potash; and, in the state of concentrated solution, form with nitrate of silver a precipitate insoluble in nitric acid; with chloride of calcium, on addition of ammonia, a crystalline precipitate; and with chloride of

	Crystals a.			Horsford.
4 C	24	....	22·65	..... 22·41
N	14	....	13·21	..... 13·05
4 H	4	....	3·77	..... 5·56
3 O	24	....	22·64	..... 21·01
SO^3	40	....	37·73	..... 37·97
	106	....	100·00	..... 100·00

	Crystals b.			Horsford.
4 C	24	....	20·87	
N	14	....	12·17	..... 12·37
5 H	5	....	4·35	
4 O	32	....	27·83	
SO^3	40	....	34·78	
	115	....	100·00	

The large quantity of hydrogen obtained in *a* renders the analysis doubtful.

Horsford likewise obtained the two following basic compounds:

Disulphate of Glycocol. — The crystals contain 25·70 per cent of C and 6·01 H, and therefore consist of $2C^4NH^5O^4,SO^3$.

Sesquibasic Sulphate of Glycocol. — *a.* The crystals contain 27·74 p.c. sulphuric acid, and therefore consist of $2C^4NH^5O^4, C^4NH^4O^3,2SO^3$. — *β.* A mixture of the solutions of *a* and *γ* yields crystals, containing 25·65 p.c. sulphuric acid and therefore $=2C^4NH^5O^4,2SO^3,HO$. — *γ.* A solution of glycocol in weak spirit, mixed with sulphuric acid even in large excess, deposits in the course of 24 hours, long rectangular prisms which are acid and permanent in the air (Horsford).

	Crystals γ dried in vacuo.			Horsford.
12 C	72	....	22·29	..... 22·58
3 N	42	....	13·00	..... 13·31
17 H	17	....	5·26	..... 5·62
14 O	112	....	34·69	..... 34·03
2 SO^3	80	....	24·76	..... 24·46
$3C^4NH^5O^4,2SO^3,2HO$	323	....	100·00	..... 100·00

Hydrochloro-saccharic Acid, or *Mono-hydrochlorate of Glycocol.* — When hippuric acid is boiled for half an hour with hydrochloric acid, the liquid left to itself till the benzoic acid has separated by cooling, and the mother-liquor decanted and evaporated, long prisms are obtained from which the glycocol may be separated by carbonate of lead. (Dessaignes). The mother-liquor evaporated to a syrup and cooled, deposits long flat prisms, which, when washed with alcohol after the mother-liquor has been decanted, are transparent and strongly lustrous; they have a sour and slightly astringent taste; are not changed by keeping them over oil of vitriol; deliquesce slowly in the air; and dissolve readily in water and hydrated alcohol, but sparingly in absolute alcohol (Horsford).

	Crystals dried over oil of vitriol.			Horsford.
4 C	24·0	....	21·54	..... 21·20
N	14·0	....	12·57	..... 12·57
6 H	6·0	....	5·39	..... 5·95
4 O	32·0	....	28·72	..... 28·34
Cl	35·4	....	31·78	..... 31·94
$C^4NH^5O^4,HCl$	111·4	....	100·00	..... 100·00

According to Horsford, there are certain *basic compounds* to be noticed under this head also.

Di-hydrochlorate of Glycocol. — *a. With comparatively little water.* — When hydrochloric acid is added to a concentrated aqueous solution of glycocol, and then a quantity of alcohol sufficient to produce a slight turbidity, crystals are formed which increase if alcohol be repeatedly dropped into the liquid; larger crystals may be obtained by slow evaporation over oil of vitriol. — Rhombic prisms; $u : u' = 87°$; of acid and sweet taste; permanent in the air.

β. With more water. — Obtained by dissolving glycocol in aqueous hydrochloric acid — which need not be used in exactly equivalent proportion—and leaving the solution to crystallize (Horsford).

Crystals a.			Horsford.
8 C	48·0	27·06	27·59
2 N	28·0	15·78	15·37
10 H	10·0	5·63	5·52
7 O	56·0	31·57	31·94
Cl	35·4	19·96	19·58
$C^4NH^5O^4 + C^4NH^4O^3,HCl$	177·4	100·00	100·00

Crystals β.			Horsford.
8 C	48·0	25·75	26·08
2 N	28·0	15·02	
11 H	11·0	5·90	6·02
8 O	64.0	34·34	
Cl	35·4	18·99	18·47
$2C^4NH^5O^4,HCl$	186·4	100·00	

Sesquibasic Hydrochlorate of Glycocol. — *a. With comparatively little water.* — 1. An aqueous solution of glycocol is mixed with excess of hydrochloric acid, and the liquid set aside to crystallize. — 2. Hydrochloric acid gas is passed to saturation over heated glycocol. The compound melts between 150° and 170°, giving off water, and generally assuming a greenish colour due to partial decomposition. The crystals obtained by (1) contain 25·43 p.c. chlorine, and the mass (2) contains 25·72 p.c.; both are therefore = $2C^4NH^4O^3,C^4NH^5O^4,HCl$.

β. With more water. — Formed in some cases by the same two processes as *a*; the crystals contain 24·59, and the fused mass obtained by heating the glycocol in hydrochloric acid gas, contains 24·23 p.c. Cl. Both are therefore = $C^4NH^4O^3,2C^4NH^5O^4,HCl$ (Horsford).

According to Mulder, glycocol dried at 100° absorbs no hydrochloric acid gas in the cold.

Nitrosaccharic Acid, or *Nitrate of Glycocol.* — Glycocol dissolves without effervescence or decomposition of any kind, in dilute nitric acid either cold or warm; and by careful evaporation and cooling, a crystalline mass is obtained amounting to much more than the glycocol used; it must be pressed between paper and recrystallized from water (Braconnot.) — Transparent, colourless, flattened, faintly striated prisms, like those of Glauber's salt, and having an acid, slightly sweetish taste (Braconnot). — In most cases, large, transparent, rhombic crystals are obtained; but sometimes the aqueous solution, when left to cool quietly, does not crystallize spontaneously, but on agitation, solidifies instantly to a mass of needle-shaped crystals (Mulder). — A solution of glycocol in

nitric acid, evaporated over oil of vitriol, sometimes yields large tables permanent in the air, and belonging to the oblique prismatic system, sometimes, especially if the liquid has been heated, needles (Horsford).

Crystals dried in vacuo over oil of vitriol at ordinary temperatures.			Boussingault.	Mulder.	Horsford.
4 C	24	17·39	17·32	18·33	17·49
2 N	28	20·29	20·20		20·51
6 H	6	4·35	4·53	4·31	4·70
10 O	80	57·97	57·95		57·30
$C^4NH^5O^4,HO,NO^5$	138	100·00	100·00		100·00

The crystals dried at ordinary temperatures in vacuo give off 4·5 p.c. water when heated to 110° in a current of air (Boussingault). [6·52 p.c. would be 1 At. water]. Heated to 120° with an excess of fixed base, they give off 3·64 p.c.; at 150°, they lose 3·13 p.c. more; and at 170°, 6·36 p.c. more; on the whole, therefore, 13·03 p.c. = 2 At. water (Mulder.)

Nitrosaccharic acid swells up strongly when heated, and detonates slightly, giving off a pungent vapour (Braconnot). It dissolves in water, but not in alcohol, not even when the alcohol is very dilute and at a boiling heat. The salts of nitrosaccharic acid deflagrate on red-hot coals like nitre.

¶ *Basic Nitrate of Glycocol.* — When 2 At. glycocol are dissolved in 1 At. dilute nitric acid, and the liquid evaporated, a viscid residue is left, which slowly changes to a crystalline mass resembling nitrate of urea. The crystals dried over oil of vitriol, contain 28·65 p.c. NO^5,HO; agreeing with the formula $2C^4NH^5O^4,HO,NO^5$. (Dessaignes, *N. Ann. Chim. Phys.* 34, 143; *Ann. Pharm.* 82, 236.) ¶.

Dry glycocol does not absorb *Ammoniacal gas*, but dissolves in aqueous ammonia.

Glycocol with Potash. — A solution of glycocol in dilute potash, evaporated to a syrup over the water-bath, yields very deliquescent needles, which must be quickly washed with alcohol. Their alcoholic solution has a strong alkaline reaction.

Glycocol with Chloride of Potassium. — The aqueous solution of glycocol and chloride of potassium, evaporated over oil of vitriol to a state of high concentration, becomes filled with delicate needles, which quickly become moist in the air, and contain 16·58 p.c. C; hence their formula is $C^4NH^4O^3,KCl$ (Horsford).

Sulphosaccharate of Potash. — When alcohol is added to an aqueous mixture of glycocol and bisulphate of potash, this salt is precipitated in translucent prisms, which, after drying over oil of vitriol, contain 30·94 p.c. sulphuric acid, and are therefore $KO,2C^4NH^4O^3,2SO^3$ (Horsford).

Nitrosaccharate of Potash. — Obtained by neutralizing nitrosaccharic acid with potash (Braconnot), or by mixing an aqueous solution of glycocol and nitre with alcohol (Horsford). Needles which taste like nitre, have a faintly sweet after-taste, and deflagrate on glowing coals like nitre (Braconnot). — Braconnot likewise distinguishes an acid salt, which also crystallizes in needles.

	Dried.			Boussingault.
KO	47·2	....	28·23	..... 27·83
4 C	24·0	....	14·35	..... 14·24
2 N	28·0	....	16·75	..... 16·61
4 H	4·0	....	2·39	..... 2·50
8 O	64·0	....	38·28	..... 38·82
$C^4NH^4KO^4,NO^5$	167·2	....	100·00	..... 100·00

Glycocol with Chloride of Sodium. — Crystallizes after some time from a concentrated aqueous solution of glycocol and common salt which has been mixed with absolute alcohol (Horsford).

Glycocol with Baryta. — When glycocol is triturated with hydrate of baryta, a semifluid mass is obtained. which, on being mixed with water and left at rest, yields after a while crystals of this compound (Horsford).

Glycocol with Chloride of Barium. — A solution of 1 At. chloride of barium and 1 At. glycocol in hot water, yields rhombic prisms on cooling, and flat needles by precipitation with alcohol. The salt is bitter, neutral and permanent in the air; contains 55·34 p.c. chloride of barium, so that its formula is $BaCl,C^4NH^5O^4,HO$ (Horsford).

Nitrosaccharate of Baryta. — 138 pts. (1 At.) of nitrosaccharic acid dried in vacuo, supersaturated with baryta-water, and then freed from excess of baryta by carbonic acid and boiling, retain 102 pts. (nearly 1½ At.) of baryta in combination (Mulder).

¶ *Glycocol with Lime.* — Glycocol boiled for some time with carbonate of lime dissolves a considerable quantity of lime (Dessaignes). ¶

Nitrosaccharate of Lime. — Aqueous nitrosaccharic acid saturated with carbonate of lime, yields on evaporation needle-shaped crystals, which are permanent in the air, sparingly soluble in water, and when thrown on red-hot coals, first melt in their water of crystallization, and then deflagrate like nitre (Braconnot).

Nitrosaccharate of Magnesia. — Uncrystallizable, deliquescent; when thrown on red-hot coals, it intumesces strongly, detonates slightly, and leaves a brown, arborescent, tumefied residue (Braconnot).

Glycocol with Chromate of Potash? — An aqueous solution of glycocol and bichromate of potash. mixed with absolute alcohol, soon yields crystals, which even when left in the liquid, decompose in a few days, with separation of carbon (Horsford).

¶ *Glycocol with Zinc-oxide.* — Zinc-oxide dissolves readily in a hot solution of glycocol, and the liquid on cooling, yields laminar crystals having a silky lustre. The crystals dried in the air contain 35·75 p.c. zinc-oxide; the formula $C^4NH^5O^4,ZnO$ requires 35·07 p c. (Dessaignes). ¶

Nitrosaccharate of Zinc. — Zinc dissolves in nitrosaccharic acid with evolution of hydrogen, and forms a crystallizable salt (Braconnot).

¶ *Glycocol with Cadmic Oxide.* — Cadmic oxide forms with glycocol a compound very much like that which glycocol forms with zinc-oxide, and containing 45·82 p.c. CdO; the formula $C^4NH^5O^4,CdO$ requires 45·94 p.c. (Dessaignes). ¶

Glycocol with Protochloride of Tin. — Crystallizes from a mixture of the saturated aqueous solutions of glycocol and protochloride of tin (Horsford).

Glycocol with Lead-oxide. — Glycocol mixed with excess of protoxide of lead, and thoroughly dried by heat, gives off 12·5 p.c. water (Mulder). [12 p.c. = 1 At.]. When protoxide of lead is boiled with aqueous glycocol, and the solution filtered and evaporated out of contact of air, colourless needles are obtained, which, after drying at 120°, give off no more water at 150°, but are decomposed by carbonic acid (Boussingault). They effloresce in vacuo (Mulder). Their solution has an alkaline reaction (Boussingault). When the filtrate obtained after boiling aqueous glycocol with lead-oxide is mixed with alcohol till it begins to be turbid, prisms are gradually formed resembling cyanide of mercury, and increasing on frequent addition of alcohol (Horsford).

	at 120°.			Muld. & Ballot.	Boussingault.
PbO	112	....	62·92	64·93	64·90
4 C	24	....	13·48	13·49	13·29
N	14	....	7·87		7·78
4 H	4	....	2·25	2·13	2·04
3 O	24	....	13·48		11·99
$C^4NH^4PbO^4$	178	....	100·00		100·00

	Crystals air-dried.			Horsford.
PbO	112	....	59·90	57·60
4 C	24	....	12·83	12·07
N	14	....	7·49	
5 H	5	....	2·67	2·10
4 O	32	....	17·11	
$C^4NH^4PbO + HO$	187	....	100·00	

Nitrosaccharate of Lead. — Obtained by dissolving lead-oxide in nitrosaccharic acid (Braconnot), or the compound of lead-oxide and glycocol in nitric acid (Boussingault). — The compound is not crystallizable, but gummy; it is permanent in the air, and deflagrates in the fire (Braconnot). — After drying at 130°, it contains 45·92 p.c. lead-oxide (Mulder), and is therefore $PbO,C^4NH^5O^4,NO^5$.

Iron behaves with nitrosaccharic acid just like zinc (Braconnot). Glycocol imparts a red-brown colour to sesquichloride of iron (Mulder).

Glycocol with Cupric Oxide. — 1. Obtained by boiling cupric oxide continuously with aqueous glycocol (Mulder). The greenish blue filtrate, when cooled after sufficient boiling, solidifies to a crystalline mass (Boussingault); it becomes filled with delicate needles of a fine blue colour (Horsford). — 2. Hydrated cupric oxide is dissolved in aqueous glycocol, and the crystals separated by addition of alcohol (Horsford). — 3. An aqueous solution of cupric sulphate and glycocol is mixed, first with potash, and then with alcohol, which when sufficiently concentrated, precipitates the compound completely (Horsford). The crystals, when heated to 100°, assume green and violet tints, and give off 8·04 p.c. (1 At.) water (Horsford). They give off water at 120°, and afterwards no more below 140° (Boussingault). After drying at 100°, they give off an additional 3·34 p.c. water at 140°, but no more at 160° (Mulder).

Anhydrous.			Mulder. at 160°.	Boussingault. at 140°.
CuO	40	37·74	37·14	37·60
4 C	24	22·64	22·83	23·57
N	14	13·21		13·92
4 H	4	3·77	3·86	3·74
3 O	24	22·64		21·17
$C^4NH^4CuO^4$	106	100·00		100·00

Crystals dried in vac. at ord. temp.			Horsford.
CuO	40	34·78	33·89
4 C	24	20·87	21·10
N	14	12·17	12·65
5 H	5	4·35	4·82
4 O	32	27·83	27·54
$C^4NH^4CuO^4 + HO$	115	100·00	100·00

Glycocol heated with acetate of copper completely expels the acetic acid (Dessaignes).

Cupric Nitrosaccharate. — Cupric oxide yields with nitrosaccharic acid, crystals which are permanent in the air (Braconnot). — The salt is likewise obtained by dissolving the compound of glycocol and cupric oxide in nitric acid. Azure-blue needles, which turn green, and give off a small quantity of water at 150°, and deflagrate between 180° and 182° (Boussingault).

Crystals dried in vac. at ord. temp.			Boussingault.
2 CuO	80	36·70	36·27
4 C	24	11·01	11·04
2 N	28	12·84	12·75
6 H	6	2·75	2·89
10 O	80	36·70	37·05
$CuO + C^4NH^4CuO^4,NO^5 + 2Aq$	218	100·00	100·00

¶ *Glycocol with Mercuric Oxide.* — A gently heated solution of glycocol rapidly dissolves mercuric oxide, and the solution on cooling, yields an aggregate of crystals, which become opaque when dry. When the aqueous solution of this compound is heated to the boiling point, carbonic acid is evolved; the liquid becomes coloured; mercury is reduced; and a number of decomposition-products are formed, among which is formiate of ammonia (Dessaignes, *Ann. Pharm.* 82, 235).

Dried in vacuo.			Dessaignes.
HgO	108	59·02	58·98
$C^4NH^5O^4$	75	40·98	41·08
$HgO,C^4NH^5O^4$	183	100·00	100·06 ¶

Glycocol with Silver-oxide. — Oxide of silver dissolves readily in hot aqueous glycocol. To obtain a saturated compound, however, the two substances must be digested together between 80° and 100° for several hours, the liquid then boiled for a few seconds, and filtered hot: the transparent crystalline grains thereby obtained are dried at 110° in a current of dry air (Boussingault). — An aqueous solution of glycocol boiled with oxide of silver, and then mixed with alcohol, yields nodular crystals, which blacken when exposed to light (Horsford).

	Dried at 110°.		Boussingault.	Boussingault *b*.
AgO	116	63·74	63·75	54·30
4 C	24	13·19	13·66	17·15
N	14	7·69	8·07	10·13
4 H	4	2·20	2·21	2·74
3 O	24	13·18	12·31	15·68
$C^4NH^4AgO^4$	182	100·00	100·00	100·00

If the aqueous solution of glycocol be not completely saturated with oxide of silver, the mother-liquor decanted from the resulting crystals and evaporated in vacuo, yields a granular mass much more soluble than the normal compound. It has the composition given under *b* in the preceding table and contains 3 At. silver-oxide to 4 At. glycocol (Boussingault).

Nitrosaccharate of Silver. — Obtained by dissolving oxide of silver in nitrosaccharic acid, or the compound of that oxide with glycocol in nitric acid, or glycocol in aqueous nitrate of silver. Beautiful needles, which quickly blacken when exposed to light; they do not detonate when heated alone (Boussingault). The crystals detonate strongly when heated; they absorb moisture when exposed to the air (Horsford).

	Crystals.		Boussingault.	Horsford.
AgO	116	49·15	48·60	49·83
4 C	24	10·17	10·08	10·19
2 N	28	11·86	11·83	
4 H	4	1·70	1·86	2·22
8 O	64	27·12	27·63	
$C^4NH^4AgO^4,NO^5$	236	100·00	100·00	

Glycocol with Bichloride of Platinum. — A concentrated solution of bichloride of platinum in excess of hydrochloric acid is added to an aqueous solution of glycocol, and absolute alcohol added by drops, whereupon the mixture becomes turbid and desposits crystals;—or the liquid, without addition of alcohol, is evaporated in vacuo over oil of vitriol. Cherry-coloured prisms which, when exposed to the air, give off water and become lighter coloured on the surface. They contain 33·03 p.c. platinum, and therefore consist of $PtCl^2, C^4NH^5O^4 + HO$. (Horsford). [Or, rather, $PtCl^2, C^4NH^5O^4 + 6HO$.]

Glycocol is insoluble in absolute *Alcohol*, even at a boiling heat, but dissolves with tolerable facility in hydrated alcohol (Braconnot). It dissolves in 930° pts. alcohol of sp. gr. 0·828; the boiling saturated solution becomes turbid on cooling (Mulder). It does not dissolve in ether (Mulder). It is nearly insoluble in absolute alcohol and in ether (Horsford).

It forms a compound which may be regarded as sulphosaccharate of ethyl, $C^4H^5O, C^4NH^5O^4, SO^3$, and contains 17·27 p.c. sulphuric acid precipitable by chloride of barium (Horsford). [The formula, to agree with the analysis, must be $C^4H^5O, 2C^4NH^5O^4, SO^3$.]

Aceto-saccharic Acid. When alcohol is added to a solution of glycocol in acetic acid till the liquid becomes turbid, crystals are produced which increase if alcohol be frequently added in small quantities; the solution may also be rapidly precipitated by a large quantity of alcohol, and the precipitate recrystallised from water (Horsford).

	Crystals.			Horsford.
8 C	48	....	33·33	..... 33·33
N	14	....	9·73	
10 H	10	....	6·94	..... 7·57
9 O	72	....	50·00	
$C^4NH^5O^4, C^4H^4O^4 + Aq$	144	....	100·00	

Oxalo-saccharic Acid. — By boiling hippuric acid with concentrated oxalic acid, and leaving the mixture to cool, crystals of benzoic acid are obtained, and a mother-liquor which yields beautiful prisms of oxalo-saccharic acid (Dessaignes). A solution of glycocol in aqueous oxalic acid yields by evaporation a radiated crystalline mass resembling Wavellite; by gradually adding alcohol to the solution, beautiful crystals are obtained, which are permanent in the air, and contain 32·02 p.c. C; therefore = $2C^4NH^5O^4, C^4O^3$ (Horsford).

β. Amidogen-nucleus C^4AdHO^2.

Oxamic Acid. $C^4NH^3O^6 = C^4AdHO^2, O^4$.

BALARD. *N. Ann. Chim. Phys.* 4, 93; also *Ann. Pharm.* 42, 196; also *J. pr. Chem.* 25, 84.

Oxaminsäure, Acide oxamique. — Discovered by Balard in 1842.

Formation (p. 123).

Preparation. Dehydrated acid oxalate of ammonia is carefully heated to incipient fusion in a tubulated retorted placed on the oil-bath; the melted portion mixed with that which is still solid, by means of a rod inserted through the tubulure, in order to diffuse the heat more uniformly, till the whole softens to a nearly fluid mass, which, as the action goes on, becomes pasty and swells up very much. As soon as the frothing ceases, and, in place of an acid distillate which gives off no ammonia when treated with potash, hydrocyanate and carbonate of ammonia begin to pass over, and produce an effervescence on coming in contact with the acid distillate, the distillation must be interrupted, and the residual porous mass—which is yellowish if the mixture has been carefully heated, but red-brown if the heat has been too quickly applied—is treated with cold water, which dissolves the oxamic acid, and sometimes also a small quantity of undecomposed acid oxalate of ammonia, leaving some coloured oxamide undissolved.

To obtain the acid in a state of greater purity, the following processes may be adopted:

1. The preceding cold aqueous solution is neutralized with ammonia; crystallized oxamate of ammonia obtained from it by evaporation and cooling; this salt dissolved in the smallest possible quantity of hot water; an equivalent quantity of sulphuric acid added; and the liquid quickly cooled, whereby the oxamic acid is precipitated in the form of a white powder. — 2. The solution neutralised with ammonia is precipitated with a saturated solution of a baryta-salt, the crystalline precipitate purified by solution in boiling water (digesting it with animal charcoal if it be coloured) and crystallization; the crystals decomposed

by an equivalent quantity of very dilute sulphuric acid; and the filtrate gently evaporated to the crystallizing point. — 3. Dry hydrochloric acid gas is passed in excess over dry and gently heated oxamate of silver, whereupon decomposition takes place, attended with great evolution of heat. The excess of hydrochloric acid is then expelled by a dry current of air; the residue boiled with absolute alcohol and filtered from chloride of silver; and the acid obtained by evaporating the filtrate, in the form of a colourless powder. If too much heat is applied in decomposing the silver-salt, the acid has a yellowish colour.

Properties. White, crystalline, granular :

				Balard.
4 C	24	26·97		26·1
N	14	15·73		16·6
3 H	3	3·37		3·9
6 O	48	53·93		53·4
$C^4NH^3O^6$	89	100·00		100·0

The hypothetical anhydrous acid is $C^4NH^3O^5$.

Oxamic acid is reconverted, by boiling its aqueous solution, into acid oxalate of ammonia:

$$C^4NH^3O^6 + 2HO = C^4(NH^4,H)O^8.$$

Combinations. The acid dissolves very sparingly in cold water.

Oxamate of Ammonia. — By boiling the baryta-salt with an equivalent quantity of sulphate of ammonia, evaporating the filtrate, and leaving it to cool, the ammonia-salt is obtained in small prisms arranged in stellate groups:

Crystals.			Balard.
4 C	24	22·64	22·3
2 N	28	26·42	26·5
6 H	6	5·66	5·8
6 O	48	45·28	45·4
$C^4(NH^2,NH^4,O^2)O^4 = C^4(Ad,Am,O^2)O^4$	106	100·00	100·0

Oxamate of Baryta. — The cold aqueous solution of the residue obtained in distilling acid oxalate of ammonia, after neutralization with ammonia, precipitates concentrated solutions of baryta-salts, but gives no precipitate with dilute solutions. (p. 259, 2.) The crystalline precipitate is purified by recrystallization from warm water. The salt heated with oil of vitriol, gives off carbonic oxide and carbonic acid gases in equal volumes, and leaves ammonia in the residue. The salt heated to 150° in a dry current of air gives off 15·45 p.c. water.

Crystallized.			Balard.
BaO	76·6	39·98	41·65
4 C	24·0	12·53	
N	14·0	7·31	
2 H	2·0	1·04	
6 O	48·0	25·05	
3 Aq	27·0	14·09	14·87
C^4AdBaO^2,O^4+3Aq	191·6	100·00	

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Oxamate of Lime. — With lime-salts also, the aqueous solution of the acid neutralized with ammonia forms a crystalline precipitate, but only when the solutions are tolerably concentrated. If the solution still contains undecomposed acid oxalate of ammonia, the precipitate becomes contaminated with oxalate of lime, which however remains behind when the oxamate of lime is dissolved in boiling water.

Oxamate of Silver. — Obtained by precipitating nitrate of silver with the aqueous solution of the ammonia or baryta-salt. The copious, translucent, gelatinous magma soon becomes opaque; it dissolves on heating the liquid, and the salt separates again on cooling in white, silky needles. These crystals blacken when exposed to light, becoming coated with metal; the same effect takes places at 150°, at which temperature no water is given off (Balard).

	Crystallized.		Balard.
4 C	24	12·25	12·23
N	14	7·14	7·29
2 H	2	1·02	1·17
Ag	108	55·10	54·99
6 O	48	24·49	24·32
$C^4(AdAgO^2)O^4$	196	100·00	100·00

¶ Methyloxamic Acid. $C^6NH^5O^6 = C^4N(H^3Me)O^5$.

WURTZ. *N. Ann. Chim. Phys.* 30, 465.

Acid oxalate of methylamine heated to 160° is resolved into 2 At. water, and 1 At. methyloxamic acid (p.172):

$$C^4(H,C^2H^6N)O^8 = C^6NH^5O^6 + 2HO.$$

The methyloxamic acid partly remains in the body of the retort, and partly volatilizes, sometimes forming a crystalline sublimate in the neck. The quantity obtained is however but small, because the greater portion of the acid salt is resolved by the heat into water, carbonic acid, carbonic oxide and neutral oxalate of methylamine, and the latter is subsequently converted into methyloxamide (p. 265). As soon as this product appears, it is best to interrupt the operation, and treat the residue with a little free oxalic acid.

The distilled product and the residue must then be dissolved in hot water, the solution saturated with chalk, and filtered. The filtrate yields on cooling a mixture of crystals of methyloxamide and methyloxamate of lime, the former of which may be easily volatilized by heat, while the latter remain unaltered. They may be purified by dissolving them in hot water and recrystallizing:

	Lime-salt.		Wurtz.
6 C	36	29·50	29·26
4 H	4	3·27	
N	14	11·47	
Ca	20	16·39	16·43
6 O	48	39·37	
$C^4N(H,C^2H^3,Ca)O^6$	122	100·00	

Ethyloxamic acid, $C^6NH^7O^6 = C^4N\left\{\begin{matrix}H^2\\C^4H^5\end{matrix}\right\}O^6$, is obtained in a similar manner by mixing neutral oxalate of ethylamine with excess of oxalic acid, and fusing the acid oxalate in the oil-bath at 180°:

$$C^4(H,C^4H^5N)O^8 = C^6NH^7O^6 + 2HO.$$

The quantity obtained is but small (Wurtz, *N. Ann. Chim. Phys.* 30, 490). ¶

γ. *Amidogen-nucleus* $C^4Ad^2O^2$.

Oxamide. $C^4N^2H^4O^4 = C^4Ad^2O^2,O^2$.

Bauhof. *Schw.* 19, 313.
Dumas. *Ann. Chim. Phys.* 44, 129; also *J. Chim. méd.* 6, 401; also *Schw.* 61, 82; also *Pogg.* 19, 474. — *Ann. Chim. Phys.* 54, 240.
O. Henry & Plisson. *Ann. Chim. Phys.* 46, 190; also *J. Pharm.* 17, 177; abstr. *Schw.* 62, 168.
Liebig. *Ann. Pharm.* 9, 11 & 129; also *Pogg.* 39, 331 & 359.
Mohr. *Ann. Pharm.* 18, 327.
Pelouze. *Ann. Chim. Phys.* 79, 104; also *J. pr. Chem.* 25, 486.
Malaguti. *Compt. rend.* 22, 852.

This compound was first obtained by Bauhof in 1817, on mixing oxalic ether with aqueous ammonia; but it was regarded as a compound of oxalic ether with alcohol, till Liebig, in 1834, showed it to be identical with the oxamide which Dumas had obtained in 1830, by distillation of oxalate of ammonia.

Formation. 1. By the decomposition of oxalate of ammonia at high temperatures (Dumas, p. 122). If the heat be interrupted before the volatilization is complete, oxamide is found in the residue; it is therefore produced before sublimation (Mohr). — 2. By mixing aqueous ammonia with oxalic ether (Bauhof, p. 180). A copious white precipitate is immediately formed; if however the oxalic ether has been previously mixed with alcohol, the formation of the precipitate does not take place for some seconds (Bauhof). A solution of oxalic ether in vinic ether likewise forms this precipitate with aqueous ammonia (Liebig).— 3. By the action of nitric acid on ferrocyanide of potassium. (Playfair, VIII. 125.)

Preparation. — When normal oxalate of ammonia is subjected to dry distillation till the residue disappears, oxamide is obtained, partly sublimed in the neck of the retort together with carbonate of ammonia, partly floating in flakes in the watery distillate. The whole is suspended in water, and the oxamide, amounting to 4 or 5 per cent of the ammonia-salt, collected on a filter, and washed with water (Dumas). — The compound may also be obtained by neutralizing binoxalate of potash with ammonia; adding sulphate or hydrochlorate of ammonia; evaporating to dryness; distilling; and washing the sublimate with water to free it from carbonate of ammonia. 100 pts. of salt of sorrel, neutralized with ammonia and mixed with 60 pts. of sulphate of ammonia, yield 8·25 pts. of oxamide, the whole of the sulphuric acid being left behind in the form of sulphate

of potash. 100 pts. salt of sorrel distilled with 50 pts. of sal-ammoniac (in which case the neutralization with ammonia may be dispensed with, because the hydrochloric acid is driven off), yield, first water, then hydrochloric acid, then oxamide with carbonate of ammonia, and 5·52 pts. of sublimed oxamide; the partially decomposed carbonaceous residue, washed with water and sublimed again, yields a little more oxamide coloured brown by empyreumatic oil (Mohr).

2. Aqueous ammonia is mixed with oxalic ether, either pure or dissolved in alcohol, and the precipitated oxamide purified with water and alcohol (Bauhof, Liebig). — Or the distillate obtained from 1 pt. salt of sorrel, 1 pt. alcohol, and 2 pts. oil of vitriol may be immediately shaken up with aqueous ammonia. The clear mixture becomes heated, and deposits oxamide, which must be washed, first with water and then with alcohol, to remove sulphovinate of wine-oil which adheres to the oxamide and imparts to it a faint ethereal odour (Liebig).

Properties. White, loose powder, soft to the touch (Bauhof). White, confusedly crystallized laminæ or granular powder (Dumas). Sometimes coloured yellowish or brownish in parts by a substance resembling paracyanogen (Dumas). — By gentle heating in an open test-tube, it may be sublimed without decompostion, in indistinct crystals or as a white powder (Dumas, Liebig). When heated in a retort, it melts partially, boils, and sublimes undecomposed in part only (Dumas). Inodorous, tasteless and neutral (Bauhof, Dumas).

	at 100°.		Dumas. (1).		(2).	Liebig. (2).	Varrentrapp & Will.
4 C	24	27·27	26·95		26·9	27·27	
2 N	28	31·82	31·67		31·9	31·58	31·7
4 H	4	4·55	4·59		4·5	4·62	
4 O	32	36·36	36·79		36·7	36·53	
$C^4Ad^2O^4$	88	100·00	100·00		100·0	100·00	

Decompositions. 1. Oxamide heated in a retort, melts and boils, but only at the hottest parts, and is partly sublimed without decomposition, partly resolved into cyanogen, and light, very flocculent charcoal (Dumas). — Only the smaller portion decomposes, yielding a small quantity of distillate, consisting of alcohol, ammonia, and empyreumatic oil (Bauhof). — Oxamide when strongly heated gives off a distinct odour of cyanic acid. The vapour passed through a red-hot glass tube 2 feet long, is completely resolved, without deposition of charcoal, into carbonic oxide, carbonate of ammonia, hydrocyanic acid and urea, which presents the appearance of an oily distillate quickly solidifying (Liebig):

$$2C^4N^2H^4O^4 = 2CO + 2CO^2 + NH^3 + C^2NH + C^2N^2H^4O^2 \text{ (Liebig).}$$

Oxamide hermetically sealed in a metal tube and heated in a bath for some minutes to 310°, is partially decomposed into cyanogen, carbonic acid and ammonia (Malaguti). The first products are probably cyanogen and water:

$$C^4N^2H^4O^4 = 2C^2N + 4HO;$$

but the water acting at 200° on another portion of the oxamide forms oxalate of ammonia:

$$C^4N^2H^4O^4 + 4HO = 2NH^3,C^4H^2O^8;$$

and the oxalate of ammonia is resolved at 220° (p. 122) into carbonic oxide and carbonate of ammonia. — Similarly, a mixture of oxamide and sand heated in a retort to 300°—330°, yields nothing but cyanogen, carbonic oxide, and carbonate of ammonia (Malaguti).

2. Oxamide kept in contact for some time with saturated chlorine-water, disappears completely, forming hydrochloric acid, oxalic acid, and probably also chloride of nitrogen, which then undergoes further decomposition, but without formation of sal-ammoniac (Malaguti).

3. Oxamide boiled with a four-fold quantity of nitric acid, of sp. gr. 1·35, is resolved into a mixture of 1 vol. nitrogen, 1 vol. nitrous oxide, and 2 vol. carbonic acid gas (Malaguti):

$$C^4N^2H^4O^4 + 2NO^5 = 2N + 2NO + 4CO^2 + 4HO.$$

According to Bauhof, nitric acid, even when hot, has no action upon oxamide; according to O. Henry & Plisson, strong nitric acid forms with it ammonia and carbonic acid. —4. With oil of vitriol, but only when heated, oxamide forms carbonic oxide and carbonic acid in equal volumes, ammonia remaining behind in combination with the sulphuric acid which remains colourless (Dumas, Liebig):

$$C^4N^2H^4O^4 + 2HO = 2CO + 2CO^2 + 2NH^3.$$

5. All the stronger acids in the dilute state decompose oxamide, yielding an ammonia-salt and free oxalic acid (O. Henry & Plisson):

$$C^4N^2H^4O^4 + 6HO + 2SO^3 = 2(NH^4O,SO^3) + C^4H^2O^8.$$

Such is the action exerted by sulphuric, hydrochloric, nitric and tartaric acid, as well as by oxalic acid itself, but not by acetic acid, which indeed when boiled with oxamide, goes off in vapour, without exerting any action (O. Henry & Plisson).

6. Oxamide is not altered by 14 days contact with cold water, or by boiling with water; but when heated with water to 224° under increased pressure, it yields a liquid which is acid after evaporation, gives off ammonia with hydrated oxide of lead, and yields an abundant precipitate with lime-salts (O. Henry & Plisson). — 7. Oxamide heated with aqueous alkalis is resolved into oxalate of potash, and ammonia which volatilizes, without any trace of alcohol. (Dumas.) This decomposition was previously observed by Bauhof, who however thought that alcohol was likewise formed:

$$C^4N^2H^4O^4 + 2HO + 2KO = C^4K^2O^8 + 2NH^3.$$

According to this equation, 100 pts. of oxamide should yield 102·28 pts. of oxalic acid ($C^4H^2O^8$), and 38·63 ammonia; Liebig obtained 102·5 pts. and 36 pts. — Aqueous ammonia decomposes oxamide, even at ordinary temperatures, gradually dissolving it in the same manner (O. Henry & Plisson). Boiling carbonate of potash, according to Bauhof, has no action upon oxamide.

The boiling aqueous solution of oxamide does not precipitate nitrate or acetate of lead; but on the addition of a small quantity of ammonia and application of heat, it throws down basic oxalate of lead (p. 154); the decomposition of oxamide into oxalic acid and ammonia takes place much more quickly under these circumstances than under the influence of acids or alkalis alone, being assisted probably by the insolubility of the lead-salt (Pelouze).

8. On gently heating oxamide in contact with potassium, cyanide of

potassium is formed, with vivid deflagration (Löwig, *Pogg.* 40, 407). Probably thus:

$$C^4N^2H^4O^4 + 6K = 2C^2NK + 4KO + 4H.$$

Combinations. — Oxamide requires 10,000 pts. of cold water to dissolve it (O. Henry & Plisson); in boiling water it dissolves somewhat better, and separates on cooling in indistinct crystalline flakes (Dumas). The aqueous solution does not precipitate lime-salts (Dumas).

¶ *Oxamide with Mercuric Oxide.* — When oxamide is boiled with water, and mercuric oxide added by small portions as long as it loses its colour, then more oxamide added, till the product becomes perfectly white, the compound is obtained in the form of a heavy white powder which must be frequently boiled with a large quantity of water to remove the excess of oxamide. It is decomposed by hydrochloric acid at a gentle heat (Dessaignes, *Ann. Pharm.* 82, 233).

				Dessaignes.
HgO	108	55·10		54·32
$C^4N^2H^4O^4$	88	44·90		45·41
$HgO,C^4N^2H^4O^4$	196	100·00		99·73 ¶

Oxamide does not combine with oxide of lead or oxide of silver (Pelouze).

It does not dissolve perceptibly in alcohol or vinic ether (Bauhof, Dumas).

¶ Methyloxamide. $C^6N^2H^6O^4 = C^4N^2(H^2Me^2)O^4$.

Wurtz. *N. Ann. Chim. Phys.* 30, 464.

Formation and Preparation. 1. Neutral oxalate of methylamine is resolved by dry distillation into water and methyloxamide:

$$C^4(C^2H^5N)^2O^8 = C^6N^2H^6O^4 + 4HO.$$

The transformation is much more complete than that of oxalate of ammonia into oxamide, because methyloxamide is much more volatile than oxamide. The methyloxamide collects in the neck of the retort in the form of long delicate needles interlacing each other in all directions. — 2. By the action of a solution of methylamine on oxalic ether, the products being alcohol and methyloxamide:

$$C^4(C^4H^5)^2O^8 + 2C^2H^5N = 2C^4H^6O^2 + C^6N^2H^6O^4.$$

This is the better mode of preparation. The reaction takes place immediately, with evolution of heat, the product being a white magma composed of delicate needles; these dissolve readily in hot water, and as the solution cools, the methyloxamide crystallizes in the form of long interlaced needles. It dissolves in alcohol less readily than in water. The fixed alkalis decompose it easily, with evolution of ammonia [methylamine] and formation of an alkaline oxalate:

$$[C^6N^2H^6O^4 + 2HO + 2KO = C^4K^2O^8 + 2C^2H^5N].$$

It is carbonized by anhydrous phosphoric acid.

	Crystallized from alcohol.			Wurtz.
8 C	48	....	41·37	..... 41·25
2 N	28	....	24·13	
8 H	8	....	6·89	..... 6·99
4 O	32	....	27·61	
$C^4N^2H^2(C^2H^3)^2O^4$	116	....	100·00	

¶ Ethyloxamide. $C^{12}N^2H^{12}O^4=C^4N^2(H^2Ae^2)O^4$.

Wurtz. *N. Ann. Chim. Phys.* 30, 490.

Obtained by methods precisely similar to those which yield methyloxamide; the reaction of ethylamine on oxalic ether affords the best mode of preparation.

Ethyloxamide is more soluble in alcohol and water than oxamide. From the alcoholic solution it crystallizes in beautiful needles. It is volatile and condenses on the surface of cold bodies in woolly crystals. Potash decomposes it, forming ethylamine and oxalate of potash:

$$[C^{12}N^2H^{12}O^4 + 2HO + 2KO = C^4K^2O^8 + 2C^4H^7N.]$$

Anhydrous phosphoric acid carbonizes it.

				Wurtz.
12 C	72	....	50·00	..... 49·83
2 N	28	....	19·44	
12 H	12	....	8·33	..... 8·55
4 O	32	....	22·23	
$C^4N^2H^2(C^4H^5)^2O^4$	144	....	100·00	¶

Allophanic Acid. $C^4N^2H^4O^6=C^4Ad^2O^2,O^4$.

Liebig & Wöhler. *Ann. Pharm.* 59, 291.

By passing cyanic acid vapour into absolute alcohol, Liebig & Wöhler obtained in 1830, a compound ether which they regarded as cyanic ether, till in 1847 they discovered that the substance thus formed is a compound of oxide of ethyl with a peculiar acid, allophanic acid, and should therefore be called allophanic ether; similarly the compound described (VII, 377), according to these chemists, as ureocarbonic ether, ought really to be regarded as allophanate of methyl [$= C^2H^3O,C^4N^2H^3O^5$]. — This acid has already been described in the methylene series as ureo-carbonic acid (VII, 377); but as it much more probably belongs to the ethylene-series, and as Liebig & Wöhler's more detailed memoir is now available, it will be as well to describe the acid again in this place. It bears to oxamide the same relation that acetic acid bears to aldehyde.

We are not acquainted with the acid itself, but only with some of its salts, which are obtained by treating methylic or vinic allophanate with alkalis dissolved in water or alcohol. The empirical formula of these salts is $C^4N^2H^3MO^6$. If then we suppose that the acid itself contains 2 At. amidogen, the salts must be supposed to have one of these two atoms replaced by an analogous compound NHM, so that their rational formula will be $C^4(NH^2,NHM)O^2,O^4$. When heated in the state of aqueous solution, they are resolved into carbonic acid, a carbonate,

and urea; when an attempt is made to separate the allophanic acid from them by means of another acid, the allophanic acid is immediately resolved into carbonic acid and urea. (See the Baryta-salt.)

Allophanate of Potash. — A solution of allophanic ether in alcoholic potash quickly deposits this salt in laminæ, resembling those of chlorate of potash.

Allophanate of Soda. — Obtained like the potash-salt, or by triturating the baryta-salt, without application of heat, with an equivalent quantity of aqueous sulphate of soda, and pouring alcohol upon the filtrate, which causes the soda-salt to crystallize out in small prisms having an alkaline reaction. The aqueous solution of the salt evaporated without heat in vacuo, leaves the salt in the form of a blue-glittering gelatinous mass; evaporated between 40° and 50°, it leaves the salt partly undecomposed, partly resolved into urea and carbonate of soda. The aqueous solution mixed with nitric acid gives off carbonic acid and deposits shining scales of nitrate of urea. It does not precipitate chloride of barium, but, when heated with it, forms an immediate precipitate of carbonate of baryta.

Allophanate of Baryta. — Obtained by dissolving methylic or vinic allophanate in baryta-water, whereby wood-spirit or alcohol is set free. The best method is to triturate allophanic ether with crystals of hydrate of baryta and baryta-water, without applying heat, till the ether disappears; filter from the remaining baryta-crystals; and set aside the filtrate for some days in a closed vessel: the baryta-salt then separates gradually in hard crystalline nodules and crusts. The crystals are then separated from the vessel under the liquid: the liquid quickly decanted; any carbonate of baryta that may have been formed, separated by elutriation; the crystals washed a few times with a small quantity of cold water; and dried on paper at the temperature of the air. — The baryta-salt has an alkaline reaction. When heated alone, it does not give off a trace of water, but evolves monocarbonate of ammonia, and leaves monocyanate of baryta in a state of transparent fusion:

$$BaO,C^4N^2H^3O^5 = NH^3,2CO^2 + C^2NBaO^2.$$

Its aqueous solution becomes turbid below 100°, gives off carbonic acid with effervescence, deposits all the baryta in the form of carbonate, and afterwards contains nothing but urea in solution:

$$BaO,C^4N^2H^3O^5 + HO = BaO,CO^2 + CO^2 + C^2N^2H^4O^2.$$

This salt, when an acid is poured upon it, is decomposed with brisk effervescence, yielding carbonic acid and urea; even carbonic acid produces this decomposition, though slowly; neither cyanic acid nor ammonia is formed. It appears then that allophanic acid, $C^4N^2H^4O^6$, when set free, is immediately resolved into $2CO^2$ and $C^2N^2H^4O^2$. Even when placed in contact with cold aqueous [sesqui?] carbonate of ammonia, it forms urea and carbonate of baryta. The aqueous solution forms at first a clear mixture with neutral acetate of lead, but after half an hour, a precipitate of carbonate of lead is formed. It does not precipitate a neutral solution of nitrate of silver. Dissolves in cold water slowly but completely (Liebig & Wöhler):

	Crystallized.		Liebig & Wöhler.
BaO	76·6	44·64	45·31
4 C	24·0	13·98	13·80
2 N	28·0	16·32	15·01
3 H	3·0	1·75	1·89
5 O	40·0	23·31	23·99
$C^4N^2H^3BaO^6$	171·6	100·00	100·00

Allophanate of Lime. — Prepared like the baryta-salt. Crystallizable; sparingly soluble in water (Liebig & Wöhler).

Allophanic Ether. $C^8N^2H^8O^6 = C^4H^5O, C^4N^2H^3O^5$.

Liebig & Wöhler. *Pogg.* 20, 395. — *Ann. Pharm.* 58, 260 & 59, 291.

Liebig. *Ann. Pharm.* 21, 195.

Vinic or Ethylic Allophanate, Allophanate of Ethyl, Allophansaures Aethyloxyd, Allophansäureäther; formerly *Cyanic ether.* For the history, vid. *Allophanic acid.*

Formation and Preparation. When cyanic acid vapour evolved by heating cyanuric acid, is passed into absolute alcohol, it is rapidly absorbed, with an evolution of heat which nearly makes the alcohol boil, and a crystalline powder is deposited, which increases in quantity on cooling. The remaining liquid is decanted from the powder, which is then washed several times with cold alcohol, and dried. The decanted liquid smells strongly at first of cyanic acid, and reddens litmus; but it loses both these properties after a while, and according to the statement in *Ann. Pharm.* 54, 370, leaves urethane when evaporated (Liebig & Wöhler). [The equation appears to be simply:

$$2C^2NHO^2 + C^4H^6O^2 = C^8N^2H^8O^6;$$

according to the radical theory, we might say that the alcohol gives up HO, in order to form with 2 At. cyanic acid, the hypothetical anhydrous allophanic acid, which then unites with the alcohol *minus* HO (oxide of ethyl) to form allophanic ether.] — 2. Anhydrous ether is saturated with cyanic acid vapour, which it absorbs without evolution of heat; and the liquid, which smells strongly of cyanic acid, mixed with half its bulk of 95 per cent alcohol; when set aside for some days, it deposits allophanic ether in regular crystals on the sides of the vessel (Liebig). — A hot alcoholic solution of urea mixed with oil of vitriol, deposits nothing on cooling (Liebig & Wöhler). — ¶ 3. Dry ammoniacal gas passed into an ethereal solution of bicarbonate of bisulphethyl, $C^6H^5S^2O^4$, forms allophanic ether in small white crystals, and an oily sulphur-compound (Debus, VIII. 447):

$$2C^6H^5S^2O^4 + 2NH^3 = C^8H^8N^2O^6 + C^4H^5S + 2S + HS + 2HO. \P$$

Properties. Snow-white, crystalline powder; crystallizes from a hot solution in alcohol or etherated alcohol, by slow cooling or spontaneous evaporation, in transparent, nacreous scales. When heated in the air, it melts to a clear liquid, which solidifies in a crystalline mass on cooling; but part of it volatilizes at the same time, in the form of an inodorous vapour which condenses in the air to bulky flakes composed of fine

needles, which fly about like flowers of zinc; a similar woolly vegetation likewise forms on the fused mass as it cools. Inodorous and without perceptible taste; neutral.

			Liebig & Wöhler.
8 C	48	36·36	35·44
2 N	28	21·21	20·51
8 H	8	6·06	6·04
6 O	48	36·37	38·01
$C^8N^2H^8O^6$	132	100·00	100·00

Former suppositions respecting the constitution of this ether: Liebig & Wöhler (*Pogg.* 20, 399); Berzelius (*Ann. Pharm.* 21, 125); Malaguti (*Ann. Chim. Phys.* 63, 198); Gerhardt (*Ann. Chim. Phys.* 72, 184). — [If we assume the existence of 2 At. amidogen in allophanic acid itself [$C^4N^2H^4O^6$], it is impossible to decompose the formula of allophanic ether, according to the usual practice of the radical theory, into vinic ether and hypothetical anhydrous allophanic acid, inasmuch as this hypothetical compound contains only 3H to 2N; whether this circumstance should be regarded as disproving the existence of 2 At. amidogen in the ether, or the above-mentioned separation of the formula, is a question which cannot at present be decided.]

Decompositions. 1. Allophanic ether heated in a retort, partly sublimes undecomposed at first, but at about 300°, boils briskly and gives off alcohol together with a small quantity of cyanic ether, which afterwards, with the alcohol, reproduces a small quantity of allophanic ether, and finally solidifies in the form of pure cyanuric acid. 100 pts. of allophanic ether thus decomposed yield 62·5 pts. of cyanuric acid [calculation gives 65·15 pts.]; it must be observed, however, that a small quantity of cyanic acid is evolved (Liebig & Wöhler):

$$3C^8N^2H^8O^6 = 3C^4H^6O^2 + 2C^6N^3H^3O^6.$$

2. The vapour given off by heating allophanic ether in the air, may be set on fire, and burns with a flame like that of cyanogen gas (Liebig & Wöhler). — The ether is decomposed by alcoholic potash or baryta water at ordinary temperatures, forming an alkaline allophanate and alcohol; when boiled with aqueous potash, it gives off alcohol and forms cyanate of potash (Liebig & Wöhler).

Combinations. Allophanic ether is nearly insoluble in cold *Water*, but dissolves with tolerable facility in boiling water; and the solution solidifies on cooling, in a mass consisting of silky needles (Liebig & Wöhler).

It dissolves in boiling dilute *Sulphuric* and *Nitric Acid*, and apparently without decomposition (Liebig & Wöhler).

It dissolves in aqueous *Ammonia*, somewhat more readily than in water, and crystallizes therefrom, free from ammonia (Liebig). When its boiling aqueous solution is mixed with neutral or basic acetate of lead, or with ammoniacal nitrate of silver, the ether crystallizes out unaltered and free from metal (Liebig).

It is somewhat soluble in *Alcohol*, but dissolves very sparingly in *Vinic Ether*, even at a boiling heat (Liebig & Wöhler).

δ. *Amidogen-nucleus* C^4AdCl^3.

Chloracetamide. $C^4NH^2Cl^3O^2 = C^4AdCl^3,O^2$.

CLOEZ. *Compt. rend.* 21, 69 & 373. — *N. J. Pharm.* 8, 340. — *N. Ann. Chim. Phys.* 17, 300.
MALAGUTI. *Compt. rend.* 21, 291 & 22, 853. — *N. J. Pharm.* 8, 232. — *N. Ann. Chim. Phys.* 16, 13 & 58.
CAHOURS. *N. Ann. Chim. Phys.* 19, 352.

Discovered by Cloez in 1845.

Formation. 1. By the action of ammoniacal gas or aqueous ammonia on perchlorovinic formiate (Cloez):

$$C^6Cl^6O^4 + NH^3 = C^4NH^2Cl^3O^2 + 2CClO + HCl.$$

2. When terchloracetic ether is distilled in a current of ammoniacal gas, — or, in a few minutes, when that compound is placed in contact with aqueous ammonia (Malaguti):

$$C^6H^5Cl^3O^4 + NH^3 = C^4NH^2Cl^3O^2 + C^4H^6O^2.$$

3. By the action of gaseous or aqueous ammonia on terchloracetic ether (Cloez):

$$C^6Cl^6O^4 + 4NH^3 = 2C^4NH^2Cl^3O^2 + 2NH^4Cl.$$

4. By treating chloraldehyde with ammoniacal gas (Malaguti):

$$C^4Cl^4O^2 + 2NH^3 = C^4NH^2Cl^3O^2 + NH^4Cl.$$

5. By the action of ammoniacal gas on perchlorovinic ether, bichlorocarbonic, perchloroxalic or perchlorosuccinic ether, all these compounds yielding chloraldehyde when heated (Malaguti). — 6. According to Cloez, chloracetamide is also formed by the action of ammoniacal gas on perchloromethylic formiate.

Preparation. The white substance obtained by either of these reactions, must be treated with water to free it from the sal-ammoniac with which it is mixed; after which the residual chloracetamide may be dissolved in ether, and crystallized therefrom by spontaneous evaporation (Cloez, Malaguti). Chloracetamide is obtained in greatest quantity from perchloracetic ether (Malaguti).

Properties. Snow-white, nacreous, crystalline laminæ, or if obtained by slow evaporation of the alcoholic solution, flat rhombic prisms (Cloez). Crystallizes from the boiling aqueous solution in rectangular tables belonging to the right prismatic system (Malaguti). Melts at 135°, part of it subliming at the same time (Cloez, Malaguti). Boils above 230°, and distils without decomposition, leaving only a trace of residue (Cloez). Boils at a temperature above 150°; sublimes in shining laminæ when quickly heated: and begins to decompose even at 150° (Malaguti). Has a tolerably pleasant aromatic odour, and a sweet taste (Cloez). Permanent in the air (Cloez).

	Crystallized.			Cloez.	Malaguti.	Cahours.
4 C	24·0	....	14·80	14·5	14·78	14·61
N	14·0	....	8·63	9·0	8·30	
2 H	2·0	....	1·23	1·2	1·40	1·24
3 Cl	106·2	....	65·48	66·0	65·50	65·11
2 O	16·0	....	9·86	9·3	10·02	
$C^4NH^2Cl^3O^2$	162·2	....	100·00	100·0	100·00	

Decompositions. 1. Chloracetamide, after fusion, begins to turn brown at 200°, and boils completely between 238° and 240°. The vapour passed through a tube heated to dull redness, yields carbonic oxide, carbonic acid, chlorine, and volatile chloride of cyanogen, together with a small quantity of phosgene, besides sal-ammoniac and charcoal. The decomposition takes place in several ways, as shown by the following equations:

$$C^4NH^2Cl^3O^2 = 2CO + 2HCl + C^2NCl;$$

$$C^4NH^2Cl^3O^2 = Cl + HCl + HO + CO + C^2NCl + C;$$

moreover, the HO thus produced may convert a portion of the chloracetamide into chloroform and carbonate of ammonia. (Malaguti, *vid. inf.*) — 2. Chloracetamide sealed up a with a small quantity of water in a glass tube, and heated to 100° [it should perhaps be 200°], is resolved into chloroform and carbonate of ammonia:

$$C^4NH^2Cl^3O^2 + 2HO = C^2HCl^3 + NH^3 + 2CO^2;$$

The formation of chloroform is by no means preceded by that of chloracetate of ammonia; for, if the tube be heated to 130°, the chloracetamide is found to be still unaltered, whereas chloracetate of ammonia heated with water is resolved into chloroform and carbonate of ammonia between 112° and 115° (Malaguti).

3. Chlorine gas, when dry, does not act upon chloracetamide, even in sunshine; but in presence of water and in sunshine, it forms chloracetamic acid $C^4NHCl^4O^2$, which, after a few days sublimes in the bottle in long needles (Cloez):

$$C^4NH^2Cl^3O^2 + 2Cl = C^4NHCl^4O^2 + HCl.$$

4. When dissolved in dilute nitric acid and evaporated, it leaves nothing but terchlorocetate of ammonia:

$$C^4NH^2Cl^3O^2 + 2HO = C^4NH^4Cl^3O^4.$$

5. Similarly, when chloracetamide is dissolved in aqueous ammonia, which takes place slowly in the cold, quickly with the aid of heat, it takes up 2 At. HO, so that the solution, when evaporated, yields large crystals of terchloracetate of ammonia (Malaguti). — 6. Triturated in the cold with hydrate of potash, it does not evolve ammonia; but when boiled with solution of potash, it gives off all its nitrogen in the form of ammonia, and forms terchloracetate of potash, which is resolved by further boiling into chloroform and formiate of potash (Cloez).

Combinations. Chloracetamide is insoluble in *Water* (Cloez); very sparingly soluble. (Malaguti.)

It dissolves readily in *Alcohol*, and very easily in *Ether* (Cloez, Malaguti).

Chloracetamic Acid. $C^4NHCl^4O^2$.

CLOEZ (1845). *N. Ann. Chim. Phys.* 17, 305; abstr. *N. J. Pharm.* 8, 341; also *J. pr. Chem.* 37, 313.

Chloracetamsäure, Chloracetaminsäure, Acide chloracétamique.

Chloracetamide moistened with a small quantity of water, and exposed to the sun in a bottle filled with chlorine, soon yields a sublimate of chloractamic acid in needles, which may be purified by crystallization from ether.

Long colourless needles, which fuse when heated, and partly sublime undecomposed. Nearly inodorous, but has a harsh and very disagreeable taste. Permanent in the air.

			Cloez.
4 C	24·0	12·21	12·1
N	14·0	7·12	7·0
H	1·0	0·51	0·8
4 Cl	141·6	72·02	71·4
2 O	16·0	8 14	8·7
$C^4NHCl^4O^2$	196·6	100·00	100·0

[If it be allowable to assume the existence of a chlorinated amidogen = NClH, the acid may be regarded as $C^4(NClH)Cl^3O^2$; as however it contains only 2O, it is not an acid properly so called, but an acid aldide.]

The acid, when boiled with aqueous potash, gives off all its nitrogen in the form of ammonia, and leaves nothing but chloride of potassium and carbonate of potash:

$$C^4NHCl^4O^2 + 2HO + 8KO = NH^3 + 4KCl + 4(KO,CO^2).$$

The acid is insoluble in water.

It dissolves without decomposition in cold aqueous alkalis, forming crystallizable salts.

The *ammoniacal* solution evaporated in vacuo leaves a white amorphous mass, which absorbs moisture from the air, and is thereby converted into highly lustrous crystalline laminæ. Its aqueous solution is neutral, and does not precipitate lead or silver-salts. — The *Potash-salt* is obtained in a similar manner.

The acid dissolves with tolerable facility in *Wood-spirit* and *Alcohol*, and very readily in *Ether* (Cloez).

ε. *Amidogen-nucleus.* C^4AdCl^2O.

Chlorosuccilamide. $C^4NH^2Cl^2O = C^4NCl^2H,HO = C^4AdCl^2O$.

MALAGUTI (1846). *N. Ann. Chim. Phys.* 16, 76.

A solution of chlorazosuccic acid in aqueous ammonia is evaporated in vacuo till it forms a syrup mixed with crystals; this mass is heated to 100°, as long as it continues to effervesce; then exhausted with ether, the

liquid filtered from sal-ammonia; and the filtrate left to evaporate spontaneously;—a syrup is thus obtained which crystallizes immediately in contact with water. The crystals are purified from sal-ammoniac by dissolving them three times in boiling water and cooling.

[Is the syrup which remains after evaporation of the ether $=C^4NHCl^2$, and is it subsequently converted into chlorosuccilamide by addition of HO? For the formation of this body and of chlorazosuccic acid $= C^6NH^2Cl^2O^2$, see the latter.]

Long delicate white silky needles, which fuse to a clear liquid between 86° and 87°, and at a stronger heat, distil over undecomposed in the form of a liquid, which on cooling solidifies in beautiful crystals, transparent at first, but afterwards becoming opaque, and assuming the appearance of asbestus. The compound after a while acquires a sweetish taste.

	Crystallized.			Malaguti.
4 C	24·0	....	20·20	..... 20·07
N	14·0	....	11·79	..... 11·73
2 H	2·0	....	1·68	..... 1·68
2 Cl	70·8	....	59·59	..... 59·45
O	8·0	....	6·74	..... 7·07
$C^4NH^2Cl^2O$	118·0	....	100·00	..... 100·00

Chlorosuccilamide treated with aqueous fixed alkalis, does not immediately give off ammonia; but after long boiling with caustic potash, it is resolved into ammonia and chlorosuccilate of potash (*vid. inf.*) — In aqueous ammonia it dissolves completely in the course of a few weeks, forming sal-ammoniac and a brown liquid.

It dissolves very sparingly in cold *Water*, readily in boiling water, and very readily in *Alcohol* and *Ether* (Malaguti).

Appendix.

Chlorosuccilic Acid.

The potash-salt of this acid is formed by boiling chlorosuccilamide with caustic potash, as long as ammonia continues to escape. It is soluble in water and alcohol. Its solution does not precipitate the salts of baryta, lime, magnesia, manganese or zinc. It forms white precipitates soluble in a large quantity of water, with acetate of lead, sulphate of copper and corrosive sublimate; with nitrate of silver it forms a magma composed of needle-shaped crystals; likewise soluble in a large quantity of water (Malaguti).

[If we suppose that chlorosuccilamide is decomposed by potash in the manner represented by the equation:

$$C^4NH^2Cl^2O + KO + 2HO = C^4Cl^2HKO^4 + NH^3,$$

then also chlorosuccilic acid must be supposed to be $=C^4Cl^2H^2O^4$, = *Bichloracetic acid*, and will therefore fill up the gap between chloracetic and terchloracetic acid.]

Conjugated Compounds of the Amidogen-nuclei.

Carbamic Ether or Urethane. $C^5NH^7O^4 = C^4AdH^5,2CO^2$.

DUMAS. *Ann. Chim. Phys.* 54, 233; also *Ann. Pharm.* 10, 284.
LIEBIG. *Ann. Pharm.* 10, 288.
LIEBIG & WÖHLER. *Ann. Pharm.* 54, 370; 58, 260.
WURTZ. *Compt. rend.* 22, 503; also *J. pr. Chem.* 38, 228; further, *Ann. Pharm.* 79. 286.
CAHOURS. *Compt. rend.* 21, 629; also *J. pr. Chem.* 36. 141.
GERHARDT. *Ann. Chim. Phys.* 72, 184. — *Précis, Chim. org.* 1, 140. — *N. J. Pharm.* 9, 320.

Urāthan, Uréthane, Kohlenvinamester. — Discovered by Dumas in 1833.

Formation. 1. By mixing chlorovinic formiate (p. 229) with aqueous or alcoholic ammonia (Dumas). For the equation vid. p. 230. — 2. By placing carbonic ether in contact with aqueous ammonia (Cahours):

$$2C^5H^5O^2 + NH^3 = C^5NH^7O^4 + C^4H^6O^2.$$

3. By saturating alcohol or ether with the vapour of cyanic acid, by which also allophanic ether is formed and crystallizes out (Liebig & Wöhler):

$$C^2NHO^2 + C^4H^6O^2 = C^5NH^7O^4.$$

4. Alcohol absorbs gaseous chloride of cyanogen abundantly, and loses the odour of that compound slowly when set aside in a closed vessel, more quickly in sunshine or when gently heated, sal-ammoniac being separated at the same time, and a liquid formed containing hydrochloric ether and urethane (Wurtz):

$$C^2NCl + 2C^4H^6O^2 = C^5NH^7O^4 + C^4H^5Cl.$$

The sal-ammoniac appears to be produced by a secondary action (Wurtz). — ¶ 5. By the action of ammonia on vinomethylic carbonate, methylic alcohol being formed at the same time (Chancel, VIII, 445):

$$C^5H^8O^6 + NH^3 = C^5NH^7O^4 + C^2H^4O^2. \P$$

Preparation. 1. A mixture of chlorovinic formiate and excess of alcoholic ammonia is distilled to dryness in vacuo, and the urethane separated from the admixed sal-ammoniac by distillation in the oil-bath; it then passes over as a colourless liquid which crystallizes on cooling. If a sample of the distillate dissolved in water produces turbidity in a solution of nitrate of silver, the distillation must be repeated (Dumas). 2. Carbonic ether is mixed with an equal volume of aqueous ammonia, and the mixture set aside in a stoppered bottle till the carbonic ether has completely disappeared, after which the liquid is evaporated in vacuo till the urethane crystallizes (Cahours). — 3. Alcohol or ether is saturated with vapour of cyanic acid, evolved by heating cyanuric acid; then left to cool, so that the greater part of the allophanic ether may crystallize out; and the mother-liquid decanted and evaporated sufficiently to cause the

and cold; also in *Alcohol* both absolute and hydrated (Dumas). — It also dissolves readily in *Ether* (Liebig & Wöhler).

¶ *Ethylurethane*, $C^{10}NH^{11}O^4 = C^6N(H^5Ae)O^4$, is formed by the action of cyanic ether upon alcohol:

$$C^4H^6O^2 + C^4H^5,C^2NO^2 = C^{10}NH^{11}O^4.$$

It may be regarded as ethylocarbamic ether (Wurtz, *Compt. rend.* 37, 180; *Chem. Soc. Qu. J.* VII, 92).

¶ Xanthamide. $C^6NH^7S^2O^2 = C^4AdH^5\{^{CS^2}_{CO^2} = Xd.$

Debus. *Ann. Pharm.* 72, 1; abstr. *Pharm. Centr.* 1850, 117, 135; *Laur. & Gerh. C. R.* 1850, 50; *Jahresber.* 1849, 419. — Further: *Ann. Pharm.* 82, 261; abstr. *Pharm. Centr.* 1853, 81; *N. Ann. Chim. Phys.* 36, 237; *N. J. Pharm.* 22, 311; *Jahresber.* 1852, 565.

Chancel. *Compt. rend.* 32, 587; *Instit.* 1851, 130; *J. pr. Chem.* 53, 111; *Jahresber.* 1851, 512.

Xanthogenamid, Urēthane sulfuré. — Discovered by Debus in 1849.

Formation. 1. By the action of ammonia on bioxysulphocarbonate of ethyl, xanthate of ammonia being also formed, and sulphur precipitated (Debus, VIII, 443):

$$2C^6H^5S^4O^2 + 2NH^3 = C^6NH^7S^2O^2 + C^4H^5(NH^4)O^2,2CS^2 + 2S.$$

2. By the action of ammonia on vinomethylic oxysulphocarbonate (Chancel, VIII, 445):

$$C^8H^8S^2O^4 + NH^3 = C^6NH^7S^2O^2 + C^2H^4S^2.$$

This action is analogous to the decomposition of vinomethylic carbonate by ammonia.

Preparation. Dry ammoniacal gas is passed into an alcoholic solution of bioxysulphocarbonate of ethyl, whereupon the liquid becomes hot, and yields a precipitate of sulphur. As soon as this precipitation is at an end, the passage of the gas is interrupted, the liquid filtered, and the filtrate evaporated to dryness in vacuo. The residue effloresces almost completely, forming small aggregated needles of xanthate of ammonia, saturated with an oily liquid which is xanthamide. The latter may be dissolved out by ether, and remains, after evaporation of the ether, in the form of an oil having an alliaceous odour and gradually solidifying below 28°. If this solid residue be dissolved in a small quantity of alcohol, and the alcohol evaporated, the compound is obtained quite pure and in large crystals. Or, the solution of bioxysulphocarbonate of ethyl, after being treated with ammonia, may be simply evaporated over the water-bath, and the residue freed from xanthate of ammonia by treating it with a small quantity of water. The remaining xanthamide may then be crystallized from alcohol as above.

The bioxysulphocarbonate of ethyl required for the preparation may be obtained by either of the processes given in Vol. VIII, p. 442, or better, by treating an alcoholic solution of potash with bisulphide of

carbon till it is nearly neutral; diluting the liquid with twice its bulk of water, and then passing chlorine through it, whereby chloride of potassium and bioxysulphocarbonate of ethyl are produced, the former remaining in solution, the latter separating in the form of a yellow oil:

$$C^4H^5KO^2,C^2S^4 + Cl = KCl + C^6H^5S^4O^2.$$

To prevent the decomposition of the latter compound by excess of chlorine, a small quantity of iodide of potassium may be added to the liquid, and the passage of the chlorine discontinued as soon as the liquid becomes brown from separation of iodine. The bioxysulphocarbonate of ethyl is then washed with water, dissolved in a mixture of 1 pt. ether and 2 pts. alcohol, and treated with ammonia as above (Debus).

Properties. Crystallizes in truncated rhombic pyramids belonging to the oblique prismatic system, and sometimes approximating to the cubical form. Plane angle of face h* nearly = 90°; $P : h = 118°$; $p : h = 105°$ hence, and also by direct measurement, $p : P = 137°$. The edge between P and p is sometimes slightly truncated. Cleavage very perfect parallel to h. The face h is often so greatly extended that the crystals appear to be reduced to tables. By slow evaporation very large crystals may be obtained (Debus). Colourless prisms (Chancel). Melts at 36° (Debus, Chancel). Sparingly soluble in water, but dissolves in all proportions in alcohol and ether; the solutions are neutral (Debus).

	Crystals dried in vac. over sulphuric acid.		Debus (*mean*).
6 C	36	34·28	34·36
N	14	13·36	12·90
7 H	7	6·66	7·70
2 S	32	30·47	32·14
2 O	16	15·23	
$C^6NH^7S^2O^2$	105	100·00	

Xanthamide may be regarded as urethane in which half the oxygen is replaced by sulphur (Chancel). According to the products obtained by its dry distillation (*vid. inf.*) it may also be regarded as a compound of cyanuric acid and mercaptan = $C^4H^6S^2,C^2HNO^2$ [or rather: $3C^4H^6S^2,C^6H^3N^3O^6$] (Debus). — Debus also proposes for it the formulæ C^4H^5O,C^2NH^2O,CS^2, and $C^4H^5O,C^2NH^2O,CO^2 + C^4H^5S,C^2NH^2S,CS^2$.

Decompositions. 1. Xanthamide exposed in a distillatory apparatus to a gradually increasing temperature is resolved into mercaptan and cyanuric acid:

$$3C^6NH^7S^2O^2 = 3C^4H^6S^2 + C^6N^3H^3O^6.$$

It began to give off gas at 110°, and boiled at 175°, giving off a colourless liquid which had a slight alkaline reaction, smelt of mercaptan and cyanic acid, became coloured by exposure to light, was insoluble in water, but mixed in all proportions with alcohol and ether. Its alcoholic solution gave with corrosive sublimate a copious white precipitate which became crystalline after a while, and was found to be a compound of mercaptide of mercury with chloride of mercury = $C^4H^5HgS^2$, HgCl. The residue in the retort was a solid greyish white mass, which, when dissolved in a small quantity of alcohol, yielded crystals of cyanuric acid (Debus). — 2. Xanthamide dissolves in strong *Sulphuric acid*, and is reprecipitated from the solution by water. The solution when heated or left to stand for some time, gives off, without blackening, a large quantity of sulphurous acid, and afterwards contains

* h, the truncation-face of the pyramid: P, p, faces of the pyramid.

besides sulphuric acid, an acid which forms a soluble salt with baryta (Debus). — 3. Xanthamide boiled for some time with *Hydrochloric acid*, in an apparatus so arranged that the volatile products condensable at about 10° were compelled to run back again, yielded sal-ammoniac, and a yellow, volatile oil, not yet further examined (Debus). — 4. *Nitric acid* acts violently on xanthamide, with evolution of nitric oxide, forming sulphuric acid and another acid not yet investigated. — 5. *Nitrous acid* vapour passed into water in which xanthamide is suspended, forms oxysulphocyanate of ethyl, C^4H^5O,C^2NSO (VIII, 490,) which partly crystallizes out and partly remains in solution, nitrous oxide being likewise evolved and sulphur precipitated (Debus).

$$C^6NH^7S^2O^2 + NO^3 = C^4H^5O,C^2NSO + NO + 2HO + S.$$

6. Xanthamide is decomposed by *Ammonia* at 150°, yielding carbonic acid, hydrosulphocyanic acid, and stinking compounds resembling mercaptan. — 7. *Potash-ley* and *Baryta-water* boiled for several hours with xanthamide, decompose it into alcohol and hydrosulphocyanic acid:

$$CN^6H^7S^2O^2 = C^4H^6O^2 + C^2NHS^2.$$

The experiment does not succeed very well with potash, because the excess of that alkali is difficult to separate from the products of the decomposition; but with baryta-water, in a distillatory apparatus so arranged that the volatile products may run back again for some hours, a distillate of alcohol is obtained, and the liquid in the retort, when freed from excess of baryta by a stream of carbonic acid, yields crystalline sulphocyanide of barium. Ammonia is also evolved during the distillation, especially at the beginning (Debus). — 8. Xanthamide in solution is decomposed by the oxides of lead, mercury, and silver, a metallic sulphide being formed and a vapour given off which strongly affects the eyes; the filtered liquid yields by distillation a small quantity of an inseparable neutral body, and a residue containing a small quantity of an ammoniacal salt, whose acid, when separated by sulphuric acid, gives out the odour of cyanic acid. — 9. When a neutral solution of *Cupric chloride* is added to an alcoholic solution of xanthamide, the liquid first assumes a blood-red colour, then becomes colourless, and yields a precipitate of amorphous sulphur; the liquid filtered from this precipitate when the action is ended, yields crystals, first of a compound of xanthamide and cuprous chloride, and then of oxysulphocyanate of ethyl (Debus, VIII, 491):

$$3C^6NH^7S^2O^2 + 4CuCl = 2(C^6NH^7S^2O^2,Cu^2Cl) + C^4H^5O,C^2NSO + 2HCl + S.$$

A similar reaction takes place when an aqueous solution of xanthamide is mixed with excess of cupric sulphate and hydrochloric acid, a white crystalline precipitate of the copper-compound being immediately produced. — 10. An alcoholic solution of xanthamide gives a white precipitate with corrosive sublimate, and a yellow crystalline precipitate with bichloride of platinum. With the greater number of metallic salts, however, solutions of xanthamide form no precipitates (Debus).

Combinations. Xanthamide unites with metallic iodides and chlorides, forming definite crystalline compounds.

Xanthamide with Cuprous Iodide. — *a.* $2C^6NH^7S^2O^2, Cu^2I = Xd^2Cu^2I$. — Obtained by mixing a solution of $3Xd, Cu^2Cl$ in hot alcohol, with a warm solution of iodide of potassium; a small precipitate is then formed,

and the liquid filtered therefrom, and left to stand for a few hours, deposits the compound *a* in concentrically grouped needles. The mother-liquor, when further evaporated, yields large laminar crystals of the compound *b* (*vid. inf.*), and lastly, xanthamide and chloride of potassium:

$$Xd^3Cu^2Cl + KI = Xd^3Cu^2I + KCl;$$

and

$$Xd^3Cu^2I = Xd^2Cu^2I + Xd.$$

The compound *a* crystallizes in broad, white needles, which are insoluble in water, but dissolve in considerable quantity in cold alcohol. The clear alcoholic solution becomes turbid when heated to the boiling point, and deposits a considerable quantity of cuprous iodide, whilst xanthamide remains in the liquid, and may be obtained in crystals from the filtrate by evaporation; but if the solution containing the xanthamide be allowed to cool in contact with the cuprous iodide, and left for some time afterwards in contact with it, recombination takes place, and the original compound Xd^2Cu^2I is reproduced. In boiling water the compound neither melts nor dissolves, but suffers partial decomposition. Heated on platinum foil it becomes liquid, and solidifies in a crystalline mass on cooling; at a higher temperature, it blackens and gives off mercaptan. When kept in closed vessels, it turns green and gives off mercaptan. Nitric acid decomposes it with violence, setting the iodine free. Hydrochloric acid also decomposes it, forming Xd^2Cu^2Cl and hydriodic acid. Potash, ammonia, and sulphocyanide of potassium act upon it in the same manner as on the corresponding chlorine-compound (*inf.*) (Debus).

				Debus.
2 Xd	210	....	52·5	
2 Cu	64	....	16·0	
I	126	....	31·5	..... 32·11
Xd^2,Cu^2I	400	....	100·0	

b. Xd^3Cu^2I. — Crystallizes from the mother-liquor, from which *a* has been deposited (*sup.*). Large laminated crystals (Debus).

The compounds $XdCu^2I$ and Xd^4Cu^2I appear likewise to exist (Debus).

Xanthamide with Cuprous Chloride. — *a*. $XdCu^2Cl$. — Formation and Preparation (p. 278). — Crystallizes in small, white, shining rhombohedral crystals, approximating to the cubical form. Heated on platinum foil, it melts to a yellow liquid, and at a higher temperature is decomposed, yielding mercaptan, CuS, &c.

Nearly insoluble in cold water and alcohol, but dissolves with tolerable facility in warm alcohol, to which it imparts a brown colour. On boiling the solution, part of the salt is deposited, with separation of sulphide of copper; the hot saturated solution deposits the greater part of the salt, on cooling, in crystals of the above-mentioned form. — Water and other liquids acidulated with hydrochloric acid dissolve a considerable quantity of this compound, which is then almost wholly precipitated on the addition of more water, or when the acid is neutralized by a base. Hydrochloric acid appears also to give stability to the compound; for when dissolved in hydrochloric acid, it does not decompose so readily

when heated as in a liquid not containing that acid. Nitric acid dissolves it, with separation of sulphur and nitrous acid. — With strong sulphuric acid it gives off a gas, and yields a blue pulverulent precipitate soluble in water. — Ammonia colours it blue, and dissolves a small quantity of it, forming a solution which turns black when heated. — Potash-ley colours it reddish-brown at first, but the colour changes to black in a few hours, with slight evolution of ammonia. — With iodide of potassium the compound *a* gives a white precipitate; and with sulphocyanide of potassium, a white precipitate consisting of cuprous sulphocyanide, Cu^2, CyS^2. — With sulphuretted hydrogen it yields sulphide of copper, hydrochloric acid and xanthamide (Debus).

				Debus.		
6 C	36·0	17·61		18·48		18·03
7 H	7·0	3·42		3·68		3·46
2 O	16·0	7·83				
2 S	32·0	15·66				16·16
N	14·0	6·85				
2 Cu	64·0	31·31		30·73		
Cl	35·4	17·32				17·68
$XdCu^2Cl$	204·4	100·00				

b. Xd^3Cu^2Cl. — 1. Obtained by adding rather more than 1 At. xanthamide to 1 At. of the compound *a* dissolved in alcohol, and leaving the liquor to evaporate. — 2. By gradually adding an alcoholic solution of cupric chloride to an alcoholic solution of xanthamide, till a drop of the former produces a faint reddish tint which soon disappears, a precipitate of sulphur is formed; the filtrate yields by slow evaporation crystals of the compound *b;* and oxysulphocyanate of ethyl remains in solution:

$$5C^6NH^7S^2O^2 + 4CuCl = 2(2C^6NH^7S^2O^2,Cu^2Cl) + 2HCl + S + C^4H^5O,C^2NSO.$$

3. By dissolving 4 At. cupric sulphate and 5 At. xanthamide in water, and adding an excess of hydrochloric acid, a crystalline precipitate is produced, consisting chiefly of Xd^2Cu^2Cl, but containing also small quantities of Xd^3Cu^2Cl, and sometimes also of Xd^4Cu^2Cl. Its alcoholic solution abandoned to spontaneous evaporation, yields these three compounds in the order just mentioned.

The compound *b* crystallizes from dilute alcoholic solutions in white, shining, oblique rhombic tables, but from strong solutions in large six-sided tables. The crystals become dull and like enamel by keeping, and when heated, fuse to a yellow liquid, which solidifies on cooling to a crystalline mass like melted nitre; at a stronger heat, complete decomposition takes place and mercaptan is evolved. — The compound is insoluble in water, but dissolves readily in alcohol, forming a solution which blackens by boiling, and deposits sulphide of copper. Potash added to the solution, throws down a white precipitate which dissolves in a slight excess of the reagent, forming a solution which deposits sulphide of copper after a few hours, and leaves a yellow oil when evaporated. Ammonia and carbonate of ammonia behave in a similar manner, but the precipitates are less soluble in excess of the reagents. Nitrate of silver forms a white precipitate which soon turns black. Iodide and sulphocyanide of potassium form white, crystalline precipitates. — Sulphate of soda produces no change in solutions of this compound. Hydrochloric

acid, nitric acid and sulphuretted hydrogen act upon it as on the preceding compound (Debus).

					Debus.
12 C	72·0	....	23·27	.....	23·31
14 H	14·0	....	4·52	.....	4·53
4 O	32·0	....	10·34		
2 N	28·0	....	9·05		
4 S	64·0	....	20·69		
2 Cu	64·0	....	20·69		
Cl	35·4	....	11·44		
Xd^2Cu^2Cl	309·4	....	100·00		

c. Xd^3Cu^2Cl. — 1. Obtained by dissolving 1 At. $XdCu^2Cl$ and 2 At. Xd, or 1 At. Xd^2Cu^2Cl and 1 At. Xd in alcohol, and leaving the solution to evaporate. The best mode of proceeding is to divide a solution of xanthamide into three parts; convert two parts into the compound *b* by the method above described; then add the last portion of the xanthamide and filter: the compound *c* crystallizes from the filtrate by spontaneous evaporation. — 2. An aqueous solution of xanthamide is strongly acidulated with hydrochloric acid, and cupric sulphate added in small portions as long as any precipitate is formed; this precipitate is then dissolved in alcohol, the solution filtered, and the filtrate left to evaporate; the crystals which first separate consist of the compound *c*. — Crystallizes in large aggregated crystals, derived from an oblique rhombic pyramid; they are transparent and lustrous at first, but after a while become dull and like porcelain. This compound melts when heated, and at a higher temperature is resolved into mercaptan, sulphide of copper, and other products not yet examined. It is nearly insoluble in cold water, but is readily dissolved by alcohol either cold or warm. The alcohol may be heated to the boiling point without decomposition. Potash and ammonia added to the solution exhibit the same reactions as with *b*. Carbonate of ammonia produces a white precipitate insoluble in excess. Sulphuric, hydrochloric, and nitric acid, sulphate of soda, and nitrate of silver, behave with *c* in the same manner as with *b*. Iodide and sulphocyanide of potassium produce no alteration in cold dilute solutions of *c*; but in strong and boiling solutions they form white, crystalline precipitates. Zinc produces no precipitate in the cold, but at a boiling heat it throws down copper, and liberates xanthamide (Debus).

					Debus.
18 C	108·0	....	26·07	.....	26·49
21 H	21·0	....	5·07	.....	4·92
6 O	48·0	....	11·58		
6 S	96·0	....	23·16		
3 N	42·0	....	10·13		
2 Cu	64·0	....	15·45		
Cl	35·4	....	8·54		
Xd^3Cu^2Cl	414·4	....	100·00		

d. Xd^4Cu^2Cl. — Obtained by dissolving 1 At. $XdCu^2Cl$, and from 3 to 4 At. Xd, in alcohol, and leaving the solution to evaporate. Large, transparent, colourless, rhombic crystals, of very complex form. Somewhat soluble in water; dissolves in alcohol much more readily than the

preceding compounds; in its behaviour with reagents, it agrees exactly with the compound *c*. (Debus).

				Debus.	
24 C	144·0	27·73	27·74	27·47	
28 H	28·0	5·39	5·44	5·30	
8 O	64·0	12·32			
8 S	128·0	24·64			
4 N	56·0	10·78			
2 Cu	64·0	12·32	13·62		
Cl	35·4	6·82			
Xd^4Cu^2Cl	519·4	100·00			

These several compounds of xanthamide with cuprous chloride are more fusible and more readily soluble in alcohol in proportion as they contain more xanthamide; when dissolved in very large quantities of alcohol, they undergo partial decomposition, being resolved into two other compounds, one containing more and the other less xanthamide. When kept for some time, even if protected from air and light, they become dull on the surface, and finally black, from separation of sulphide of copper (Debus).

Xanthamide with Cuprous Sulphocyanide. — *a*. $Xd,10Cu^2CyS^2$. — Sulphocyanide of potassium, added to an alcoholic solution of the compound Xd^3Cu^2Cl, throws down this compound in the form of a crystalline precipitate, which must be washed, first with alcohol, then with water, and dried. — Heated to 200° in a glass tube, it does not fuse or undergo any alteration of appearance, but gives off a small quantity of mercaptan. At a red heat, it turns black. Sulphuretted hydrogen decomposes it, yielding sulphide of copper, hydrosulphocyanic acid and xanthamide (Debus).

	Dried over oil of vitriol.		Debus.
26 C	156	11·77	11·63
7 H	7	0·53	0·76
2 O	16	1·20	
22 S	352	26·56	
11 N	154	11·65	
20 Cu	640	48·29	48·26
$C^6NH^7S^2O^2,10Cu^2C^2NS^2$	1325	100·00	

The mother-liquor obtained in the preparation of this compound contains cuprous sulphocyanide and the greater part of the xanthamide. If the precipitate *a*, instead of being immediately separated by filtration, be left for several days in contact with the mother-liquor, it absorbs more xanthamide, and forms compounds, varying in constitution according to the time of contact and the dilution of the liquid (Debus)

b. $Xd^2,3Cu^2CyS^2$. — Sulphocyanide of potassium produces no precipitate in a cold dilute alcoholic solution of Xd^3,Cu^2Cl. But if the solutions be warm and concentrated, the compound *b* is instantly precipitated in small white tables, while the greater part of the xanthamide, together with a small quantity of cuprous sulphocyanide, remains in the mother-liquor. — The compound *b*, when gently heated on platinum foil, fuses and gives off mercaptan. It is insoluble in water and in alcohol (Debus).

				Debus.
18 C	108	....	18·75	..... 18·91
14 H	14	....	2·43	..... 2·41
4 O	32	....	5·56	
10 S	160	....	27·78	
5 N	70	....	12·15	
6 Cu	192	....	33·33	..... 34·24
$2C^6NH^7S^2O^2,3Cu^2C^2NS^2$	576	....	100·00	

c. $XdCu^2CyS^2$. — When the crystals of *b* are left in their mother-liquor for a few days, they increase in size, become yellowish, take up an additional quantity of xanthamide, and are converted into the compound *c*.

				Debus.
8 C	48	....	21·15	..... 22·22
7 H	7	....	3·08	..... 3·45
2 O	16	....	7·05	
4 S	64	....	28·19	
2 N	28	....	12·34	
2 Cu	64	....	28·19	..... 27·02
$C^6NH^7S^2O^2,Cu^2C^2NS^2$	227	....	100·00	

The amount of copper found by analysis is too small, the amounts of carbon and hydrogen too great, because the compound analysed was contaminated with a small quantity of another compound containing more than 1 At. Xd to 1 At. Cu^2CyS^2.

The compound *c* fuses readily when heated in a glass tube. It does not dissolve or melt when immersed in hot water or alcohol. An alcoholic solution of xanthamide dissolves it readily, and yields by evaporation crystals of the above-mentioned compound richer in xanthamide. — Strong nitric acid acts upon it in the same manner as on other compounds of sulphocyanogen. — Hydrochloric acid eliminates hydrosulphocyanic acid, and produces the compound $XdCu^2Cl$:

$$Xd,Cu^2CyS^2 + HCl = HCyS^2 + XdCu^2Cl.$$

An alcoholic solution of potash dissolves it, forming a red solution; the liquid on exposure to the air gradually loses its colour, and deposits a brown precipitate containing copper, leaving in solution sulphocyanide of potassium, together with other products of decomposition. Sulphuretted hydrogen decomposes it, yielding xanthamide, hydrosulphocyanic acid, and sulphide of copper (Debus).

All the compounds of xanthamide with cuprous sulphocyanide turn green by keeping, and are resolved into other products not yet examined (Debus).

An alcoholic solution of xanthamide forms with *Mercuric chloride* a copious white precipitate, partially soluble in water and alcohol. When examined by the microscope, it is found to consist of crystals and amorphous matter. It contains 12 At. mercury to 1 At. carbon (Debus).

Platinum-compound. — $XdPtCl + XdPtCl^2$. — An alcoholic solution of xanthamide mixed with bichloride of platinum deposits after a few minutes a yellow crystalline precipitate, and the liquid filtered therefrom continues for several days to deposit the same compound in crystalline laminæ. The last portions, however, which crystallize out are not pure, but are contaminated with a dark brown substance, probably sulphide of platinum. The dark-coloured mother-liquor which remains after the separation of these deposits, gives off

hydrochloric acid when evaporated; yields a brown oil, which gradually volatilizes, together with the aqueous and alcoholic vapours; and leaves a dark-coloured substance, which appears to be sulphide of platinum, together with sal-ammoniac.

Dried in vac. over oil of vitriol.			Debus.		
12 C	72·0	14·00	13·97	13·39	
14 H	14·0	2·72	2·69	2·72	
4 O	32·0	6·22			
4 S	64·0	12·44		13·35	
2 N	28·0	5·45			
2 Pt	198·0	38·51	38·04	38·26	37·85
3 Cl	106·2	20·66	19·08	23·30	
$Xd^2Pt^2Cl^3$	514·2	100·00			

This compound begins to decompose at 120°, giving off a stinking oil. It is insoluble in water, alcohol, and ether. Oil of vitriol does not act upon it at ordinary temperatures, and very little even when heated. Neither is it acted upon by hydrochloric or nitric acid, but aqua-regia dissolves it readily. Potash has no action upon it (Debus). ¶

Taurin. $C^4NH^7S^2O^6 = C^4AdH^5,2SO^3$.

L. Gmelin. *Tiedemann & Gmelin. Die Verdauung*, 1, 43 and 690.
Demarcay. *Ann. Pharm.* 27, 286.
Pelouze & Dumas. *Ann. Pharm.* 27, 292.
Redtenbacher. *Ann. Pharm.* 57, 170; 65, 37.
Gorup-Besanez. *Ann. Pharm.* 59, 130.

Sources. In the bile of oxen and other animals, where, according to Strecker, it exists as the copula in gallic or choleic acid.

¶ *Formation.* By the action of heat on isethionate of ammonia, this salt when heated to 230°, giving off 2 At. water, and being converted into taurin (Strecker, *Compt. rend.* 38, 637):

$$C^4H^5(NH^4)O^2,2SO^3 = C^4NH^7S^2O^6 + 2HO. \text{ ¶}$$

Preparation. 1. Ox-bile is mixed with a large quantity of hydrochloric acid; the mixture filtered from the gummy precipitate, and evaporated till it is resolved into a tough resinous mass and an acid watery liquid. The acid liquid, when decanted and further evaporated—during which process it repeatedly deposits resinous masses, from which it must be each time decanted—yields on cooling, a quantity of taurin-crystals mixed with common salt, from which the taurin must be mechanically separated and purified by crystallization. All the resinous masses separated in the process, when dissolved in a small quantity of absolute alcohol, and filtered after cooling, leave upon the filter an additional quantity of taurin in small crystals, which may be purified by washing with absolute alcohol, and crystallized from a hot aqueous solution (Gm.). Demarçay proceeds in a similar manner, excepting that he evaporates the acid liquid decanted from the resinous mass, till the greater part of the chloride of sodium has crystallized out of it; mixes the mother-liquor with six times its bulk of alcohol; sets it aside; washes the crystallized taurin with alcohol; and recrystallizes it from boiling water.

2. Ox-bile in the crude state, or freed from the greater part of the colouring matter by animal charcoal, but mixed with a small quantity of

intestinal mucus, is exposed to the air for three weeks at a temperature of 31° to 37°, till it distinctly reddens litmus; it is then precipitated by acetic acid; the filtrate, together with the wash-water, evaporated to dryness; the residue exhausted with 90 per cent alcohol; the insoluble portion dissolved in hot water; and the filtrate left to crystallize (Gorup-Besanez). The preparation of taurin by the putrefaction of ox-bile is likewise recommended by Buchner (*J. pr. Chem.* 46, 147; *Chem. Gaz.* 1849, 189). —

¶ 3. By heating isethionate of ammonia. This salt begins to lose weight at 200°, and at 230° gives off water amounting to 11 p.c. of its weight. The fused mass is then dissolved in water, and the solution precipitated by alcohol. This precipitate when redissolved in water, yields by spontaneous evaporation, large crystals of taurin exactly resembling in appearance and properties those prepared from bile (Strecker). ¶

Properties. Large, transparent, colourless prisms belonging to the right prismatic system. *Fig.* 66, often with *p*-faces, but without the faces between *a* and *t*; $u : u' = 68° 16'$. Heavier than water, lighter than oil of vitriol. Grates between the teeth. Inodorous; has a fresh but otherwise not decided taste; no action on vegetable colours. Permanent in the air, and unalterable at 100° (Gm.). Neither melts nor decomposes at 240° (Strecker).

			Redtenbacher.	Besanez.	Demarçay.	Pelouze & Dumas.
4 C	24	19·2	19·28	18·92	19·57	19·18
N	14	11·2	11·25	11·32	11·20	11·19
7 H	7	5·6	5·73	5·77	5·68	5·63
2 S	32	25·6	25·70	26·48		
6 O	48	38·4	38·04	37·51	63·55	64·00
$C^4NH^7S^2O^6$	125	100·0	100·00	100·00	100·00	100·00

Demarçay and Pelouze & Dumas overlooked the sulphur, which Redtenbacher discovered. Heintz (*Pogg.* 71, 150) found 25·55 p.c. S; Varrentrapp & Will (*Ann. Pharm.* 39, 279) found 11·00 p.c. N. — Redtenbacher assigns to taurin the rational formula: $NH^3,C^4H^4O^2 + 2SO^3$, according to which it should be a bisulphite of aldehyde-ammonia. This view of its constitution is supported by the formation of sulphite of potash on heating taurin with potash; but the behaviour of taurin with heated oil of vitriol, nitric acid, and aqua regia leads to a different conclusion (*vid. inf.*). Redtenbacher likewise succeeded in preparing artificially a bisulphite of aldehyde-ammonia (p. 287.) which however exhibited totally different properties. — Taurin should perhaps rather be regarded as sulphate of ethylamine $C^4H^5Ad,2SO^3$, corresponding exactly to sulphate of methylamine or sulphomethylane, $C^2H^3Ad,2SO^3$.

Decompositions. 1. Taurin subjected to dry distillation, melts, turns brown, swells up strongly, and yields a brown thick empyreumatic oil, together with a small quantity of colourless, watery liquid, having a sweetish, empyreumatic odour, and containing ammonia, together with a large excess of acetic acid (Gm.). — 2. In the open fire it melts and forms a thickish liquid; swells up, and emits a sweetish empyreumatic odour like that of heated indigo, but pungent at the same time; and leaves a tumefied charcoal which burns easily and without residue (Gm.).

3. Dry chlorine gas does not act upon taurin in the cold; but when the taurin is heated in a stream of the gas till decomposition takes place, a small quantity of liquid passes over containing sulphuric acid (Redten-

bacher). — 4. Its solution in oil of vitriol, heated to the boiling point, assumes a dark colour, but without giving off sulphurous acid gas, and does not become turbid on the addition of water (Gm.). — A mixture of taurin with solution of sugar and oil of vitriol, assumes when heated, first a yellow, and then a brown-red colour (Besanez). — It is not decomposed by boiling and evaporation with strong nitric acid (Gm.). Neither is it decomposed by boiling with aqua-regia, not even on the addition of chlorate of potash, the liquid not giving a precipitate with baryta even after long boiling. But taurin burned with nitre in a red-hot crucible, yields sulphate of potash (Redtenbacher).

5. When taurin is slowly evaporated to dryness with caustic potash, all the ammonia goes off at a certain stage of the process, in the form of nitrogen, without blackening; and the residue, if cooled immediately after the evolution of ammonia has ceased, and then mixed with dilute sulphuric acid, gives off sulphurous acid gas free from sulphuretted hydrogen, and without precipitation of sulphur; this residue also, when distilled, yields sulphurous and acetic acid, with a residue of pure sulphate of potash (Redtenbacher). [The evolution of ammonia takes place with strong intumescence, and is attended with evolution of hydrogen. Hence the equation is:

$$C^4NH^7S^2O^6 + 3KO + HO = NH^3 + 2H + C^4H^3KO^4 + 2(KO,SO^2).]$$

On the other hand, when taurin is thrown into melted potash, the mass treated, after cooling, with dilute sulphuric acid, yields sulphurous and sulphuretted hydrogen gases, together with a precipitate of sulphur (Redtenbacher). At a higher temperature, the acetate of potash seems to exert a reducing action on the sulphite. —Taurin is not altered by boiling with baryta-water (Redtenbacher).

¶ 6. Taurin undergoes fermentation in contact with intestinal mucus (which acts as the ferment) and an alkaline base, such as bicarbonate of soda, but not under the influence of the ferment or the alkali alone. The liquid when left for some days in a warm place, emits a putrid ammoniacal odour, and yields carbonate of ammonia and sulphurous acid, which escapes on the addition of a stronger acid. The quantity of sulphurous acid in the liquid increases for some weeks, but afterwards diminishes, as the sulphite of soda is converted by contact with the air into sulphate. The products of the fermentation of taurin are in fact the same as those which it yields under the influence of strong alkalis (*vid. sup.*), the taurin being resolved into sulphurous acid, aldehyde or its elements (which is converted by oxidation into acetic acid, and this again during the fermentation into carbonic acid), and ammonia (Buchner, *Ann. Pharm.* 78, 203; *Jahresber.* 1851, 375). ¶.

Combinations. — Taurin dissolves in 15·5 pts. of *Water* at 12°, and in a smaller quantity of hot water, from which it crystallizes on cooling (Gm.).

It dissolves slowly in cold *Oil of Vitriol*, forming a clear, pale brown, thickish liquid, which does not become turbid on the addition of water (Gm.).

It dissolves in fuming *Nitric acid*, without evolution of gas, remaining unaltered after the evaporation of the acid (Gm.).

The aqueous solution exhibits no reaction with hydrochloric acid, nitric acid, ammonia, potash, lime-water, alum, protochloride of tin,

sesquichloride of iron, sulphate of copper, corrosive sublimate, mercurous nitrate, or nitrate of silver, excepting that the last-mentioned mixture, when exposed for some days to the light, assumes a brownish red colour, and deposits a few flakes (Gm.). — The aqueous solution does not act upon ammonio-nitrate of silver (Redtenbacher).

Appendix.

Bisulphite of Aldehyde-ammonia. $NH^3,C^4H^4O^2+2SO^2$.

Redtenbacher (1848). *Ann. Pharm.* 65, 37.

Preparation. 1. The alcoholic solution of aldehyde-ammonia absorbs sulphurous acid gas passed through it, in large quantity and with evolution of heat; and when it begins to turn acid, yields, if well cooled, a copious white crystalline precipitate. — 2. Alcohol saturated with sulphurous acid may also be added to alcoholic ammonia till acid reaction is produced. The crystals, after being washed on a filter with strong alcohol and dried in vacuo, are almost pure, provided pure aldehyde-ammonia has been used.

Properties. Small white needles, tasting slightly of sulphurous acid and of aldehyde-ammonia, and having an acid reaction.

			Redtenbacher.
4 C	24	19·2	19·25
N	14	11·2	11·98
7 H	7	5·6	5·81
2 S	32	25·6	
6 O	48	38·4	
$C^4NH^7S^2O^6$	135	100·0	

Therefore metameric with taurin.

Decompositions. 1. The compound enclosed in a tube does not undergo any alteration at 100°; at 120° to 140°, it turns yellowish, and when the tube is opened emits an odour of sulphurous acid. — 2. Heated on platinum foil it turns brown, blackens, swells up, gives off an odour like that of burnt taurin, and leaves a spongy charcoal. — 3. In the dry state it changes but slowly in cold air; but at 100°, it diminishes considerably in weight, turning yellow and then brownish, and emitting an odour of burnt taurin. — 4. With the stronger acids it gives off sulphurous acid gas having an odour of aldehyde, whilst an ammoniacal salt remains behind. — 5. Heated with potash it exhibits the reaction of aldehyde. — 6. Its aqueous or alcoholic solution evaporated in vacuo, yields only a few crystalline crusts, and a large quantity of tenacious gummy matter; the alcohol distilled from the alcoholic solution contains sulphurous acid. Even when the saturated aqueous solution is mixed with excess of strong alcohol, only a thick syrup is precipitated, in which a few crystals form after some time. — 7. The aqueous solution forms with baryta, lead, and silver salts, precipitates, which are wholly or partially soluble in acids. The silver-precipitate is not blackened, contains mere traces of organic

matter, and yields by ignition even more silver than monosulphite of silver.

Combinations. — Sulphite of aldehyde-ammonia dissolves readily in water, easily in hydrated, but sparingly in absolute alcohol (Redtenbacher).

Carbothialdine. $C^5NH^5S^2=C^4AdH^3,CS^2$.

Redtenbacher & Liebig (1848). *Ann. Pharm.* 65, 43.

When sulphide of carbon is added to an alcoholic solution of aldehyde-ammonia, the liquid becomes strongly heated, loses its alkaline reaction, and after a few minutes, deposits white, highly lustrous needles, which must be washed with a small quantity of alcohol.

			Redtenb. & Liebig.
5 C	30	37·04	36·87
N	14	17·28	17·16
5 H	5	6·17	6·39
2 S	32	39·51	39·64
$C^5NH^5S^2$	81	100·00	100·06

Carbothialdine dissolves instantly in dilute hydrochloric acid, and may be precipitated therefrom by ammonia or fixed alkalis, without decomposition and in the crystalline state. But the hydrochloric acid solution, when left to stand for some time, coagulates in the form of a whitish yellow paste, insoluble in water. Carbothialdine boiled with excess of hydrochloric acid, is resolved into sal-ammoniac, aldehyde, and sulphide of carbon. Oxalic acid added to a hot alcoholic solution immediately throws down capillary crystals of oxalate of ammonia. The alcoholic solution forms with copper salts a thick green precipitate; with corrosive sublimate, thick curdy flakes; and with nitrate of silver, a greenish black precipitate, which soon changes to black sulphide of silver (Redtenbacher & Liebig).

Oxamethane. $C^8NH^7O^6=C^4AdH^5,C^4O^6$.

Dumas & Boullay. *Ann. Chim. Phys.* 37, 40; also *J. Pharm.* 14, 131.
Dumas. *Ann. Chim. Phys.* 54, 241.
Liebig. *Pogg.* 31, 359. — *Ann. Pharm.* 9, 129.

Oxalvinamester, Oxamäthan, Weinkohlensäures oder ätheroxalsaures Ammoniak, Aetheroxamid, Oxaméthane, Oxalovinate d'Ammoniaque, Oxalate d'Ethyle et d'Ammoniaque, Oxamate d'Ethyle. — Discovered by Dumas & Boullay in 1823, more accurately investigated by Dumas & Liebig.

Formation (p. 180). — Cannot be prepared with oxamic ether and alcohol (Balard).

Preparation. Perfectly dry ammoniacal gas is passed through the tubulure of a retort containing perfectly dry oxalic ether, till the liquid solidifies; the mass pressed out between blotting paper, and dissolved in

Combinations. Oxamethane dissolves in *Water* in all p
and crystallizes out unaltered as the water evaporates (Li
dissolves very sparingly in cold, somewhat more freely in
(Dumas & Boullay). The aqueous solution precipitates nei
salts (Liebig), nor lead and mercury salts (Dumas & Boullay).

It dissolves in all proportions in *Alcohol*, from which it c
out (Liebig); it dissolves in alcohol more readily than in water
Boullay).

Chloroxamethane. $C^5NH^2Cl^5O^6 = C^4AdCl^5, C^1O^6$.

MALAGUTI (1840). *Ann. Chim. Phys.* 74, 304; also *J. pr.*
205. — *N. Ann. Chim. Phys.* 16, 49; also *J. pr. Chem.* 35

Chloroxamäthan, Chloroxäthamid, Chloroxaméthane, Chloroxéthami

Formation (p. 244).

Preparation Pulverized perchloroxalic ether contained
lated retort is completely saturated with dry ammoniacal gas;
mass dissolved in ether; the solution filtered from sal-ammonia
crystals which form when the ether evaporates, pressed betw
and purified by solution in hot water, treatment with anima
and repeated crystallization (Malaguti).

Properties. Chloroxamethane crystallizes from its aqueo
on cooling in white needles; but from its alcoholic solution b
tion, in the form of snow composed of needles and laminæ
The crystals belong to the right prismatic system (*Fig.* 55,
with the edges between u and t truncated). $u : u' = 85°$ 2
132° 40′; t : the face between t and $u = 151° 40$; $i : t = 125°$
last-mentioned angle is therefore the same as in oxametha
which differ may be deduced from the same primary form
oxamethane; accordingly oxamethane and chloroxamethane a
isomorphous (Prevostaye, *Ann. Chim. Phys.* 75, 322). — Chloro
melts at 134°, a large portion subliming at the same time as a
liquid, which solidifies on cooling in a slightly coloured crysta
its boiling point is above 200°. — It tastes very sweet, an
bitter after-taste only when it is not quite pure (Malaguti):

	Sublimed.			Malaguti.
8 C	48	16·61		16·85
N	14	4·84		4·84
2 H	2	0·69		0·74
5 Cl	177	61·25		60·79
6 O	48	16·61		16·78
$C^5NH^2Cl^5O^6$	289	100·00		100·00

Gerhardt (*Précis Chim. org.* 1, 119) and Malaguti suppose that the c
chloroxamethane is different from that of oxamethane, and that the two
ferent types, because they exhibit different reactions with aqueous ammoni
for this reason they altered the name to *Chloroxethamide*.

Decompositions. 1. Chloroxamethane boiled with aque
gives off a large quantity of ammonia, and forms chloride of

together with another chlorinated salt which does not precipitate nitrate of silver. When perfectly pure, it yields only a trace of oxalate of potash, but that whichhas a bitter after-taste yields rather more. — 2. It dissolves completely in aqueous ammonia in the course of a few days, forming chloroxalovinate of ammonia (Malaguti, p. 245):

$$C^8NH^2Cl^3O^6 + 2HO = NH^4O,C^4Cl^3O,C^4O^6.$$

Combinations. Chloroxamethane dissolves sparingly in cold, readily in boiling *Water*. The solution does not precipitate lime or silver-salts. —It dissolves in *Alcohol* and *Ether* (Malaguti).

¶ Compound Ureas.

WURTZ. *Compt. rend.* 32, 414; *Ann. Pharm.* 80, 346; *J. pr. Chem.* 53, 44; *Pharm. Centr.* 1851, 487, *Jahresber.* 1851, 384.

ETHYL-UREA. $C^6N^2H^8O^2 = C^2N^2(H^3Ae)O^2$. — Formed by the action of ammonia or cyanic ether:

$$C^4H^5,C^2NO^2 + NH^3 = C^6N^2H^8O^2.$$

Dissolves readily in water and in alcohol, and crystallizes from the alcoholic solution in large prisms, which decomposed at 200°, with evolution of ammonia and formation of other products not yet examined. The aqueous solution is decomposed by chlorine, forming a heavy liquid which sometimes crystallizes gradually. Nitric acid added to the aqueous solution does not form a precipitate; but the mixture, when evaporated in vacuo, yields crystals of nitrate of ethyl-urea.

METHYLETHYLUREA. $C^8N^2H^{10}O^2 = C^2N^2(H^2MeAe)O^2$. — Formed by the action of methylamine on cyanate of ethyl:

$$C^4H^5,C^2NO^2 + C^2H^5N = C^8N^2H^{10}O^2.$$

It is very deliquescent.

DIETHYL-UREA. $C^{10}N^2H^{12}O^2 = C^2N^2(H^2Ae^2)O^2$. — Formed by the action of water on cyanate of ethyl (VIII, 487):

$$2(C^4H^5,C^2NO^2) + 2HO = 2CO^2 + C^{10}N^2H^{12}O^2.$$

Also by the action of ethylamine on cyanate of ethyl:

$$C^4H^5,C^2NO^2 + C^4H^7N = C^{10}N^2H^{12}O^2.$$

The aqueous solution mixed with nitric acid and evaporated on the water-bath, yields nitrate of diethylurea, $C^{10}N^2H^{12}O^2,NHO^6$, in flattened rhombic prisms, which are very acid and deliquescent (Wurtz).

TETRETHYL-UREA. $C^{18}N^2H^{20}O^2 = C^2N^2(C^4H^5)^4O^2 = C^2N^2Ae^4O^2$. Obtained by the action of cyanic acid on oxide of tetrethylium:

$$(C^4H^5)^4NO + C^2NO = C^{18}N^2H^{20}O^2.$$

This compound is crystalline (Hofmann, *Ann. Pharm.* 78, 274).

¶ Othyl-urea. $C^6N^2H^4O^4 = C^2N^2\left\{\begin{matrix}H^3\\C^4H^3O^2\end{matrix}\right\}O^2$.

N. Zinin. *J. pr. Chem.* 62, 363.

Acetyl-urea, Acetureïd.

Formation. By the action of chloride of othyl (p. 195) on urea:

$$C^2N^2H^4O^2 + C^4H^3O^2,Cl = HCl + C^2N^2(H^3,C^4H^3O^2)O^2.$$

Preparation. Chloride of othyl poured upon dried urea acts upon it immediately without application of external heat; the mixture becomes heated; melts; the excess of chloride of othyl volatilizes; and the liquid, after being stirred for some time, assumes the form of a white, tenacious mass, which, if heated for a few minutes to 120°, entirely loses the odour of chloride of othyl; it likewise remains soft, and is afterwards scarcely diminished in weight by washing with ether. On dissolving the residue in hot alcohol and leaving the solution to cool, the othyl-urea crystallizes out. — An excess of urea appears to be advantageous in the preparation; the best proportion is 2 At. urea to 1 At. chloride of othyl.

Properties. Crystallizes from the alcoholic solution in long, four-sided needles with rectangular base; they are generally longitudinally striated, and have cavities on their surface, or four-sided grooves running along one of the two broader faces. The crystals are white with a silky lustre, and resemble those of urea. From the aqueous solution, the compound crystallizes, partly in six-sided prisms, partly in four-sided prisms with rhombic bases and dihedral summits, and collected in plumose or stellate groups.

	Dried at 120°.				Zinin.
6 C	36	....	35·29	.....	35·56
2 N	28	....	27·45	.....	27·05
6 H	6	....	5·88	.....	5·92
4 O	32	....	31·38	.....	31·47
$C^2N^2(H^3,C^4H^3O^2)O^2$	102	....	100·00	.....	100·00

Decompositions. Othyl-urea heated on platinum-foil gives off a white vapour, the crystals becoming covered with a woolly deposit; at a stronger heat it volatilizes without residue. When it is heated in a tube, the woolly deposit begins to form at 160°, but the quantity of it produced is but small, even at 200°, at which temperature the body fuses to clear liquid. This liquid solidifies on cooling, in a crystalline mass which dissolves in alcohol and water; the alcoholic solution yields crystalline geodes, composed of short, rather thick, acuminated rhombic prisms. If the heat be further raised, but not too high, and continued for some time, the compound is resolved into cyanuric acid which takes the form of needle-shaped crystals, and othyl-amine (acetamide, p. 246), which partly remains inthe liquid amongst the crystals of cyanuric acid, and partly collects on the colder parts of the vessel in the form of a woolly acicular deposit:

$$\underbrace{3\left(C^2N^2\left\{\begin{matrix}H^3\\C^4H^3O^2\end{matrix}\right\}O^2\right)}_{\text{Othyl-urea}} = \underbrace{C^6N^3H^3O^6}_{\text{Cyanuric acid.}} + \underbrace{3\left(N\begin{matrix}H^2\\C^4H^3O^2\end{matrix}\right)}_{\text{Othylamine.}}$$

2. Boiled with caustic potash, it gives off ammonia, and yields a residue of carbonate and acetate of potash:

$$C^2N^2\left\{\begin{matrix}H^3\\C^4H^3O^2\end{matrix}\right\}O^2 + 3KHO^2 = 2(KO,CO^2) + C^4H^3KO^4 + 2NH^3.$$

Combinations. Othyl-urea is soluble in *Water*; sparingly soluble in cold *Alcohol*, more readily in boiling alcohol; but less so than in water. 1 pt. of it dissolves in 10 pts. of boiling alcohol, but the solution after cooling retains only one per cent (Zinin).

¶ Cyanic Amides.

Cahours & Cloez. *Compt. rend.* 38, 314; *Chem. Soc. Qu. J.* VII, 184.

Ammonia and the compounds ammonias are acted upon by gaseous chloride of cyanogen in a manner which may be represented by the general formula

$$2C^mH^nN + C^2NCl = C^mH^nN,HCl + C^mH^{n-1}N,C^2N.$$

the products being a hydrochlorate of the base, and a compound o cyanogen, with the amide corresponding to that base. Thus when a mixture of ammonia and chloride of cyanogen carefully dried is passed into anhydrous ether, sal-ammoniac separates out and cyanamide (VIII, 145) is formed, which remains dissolved in the ether:

$$2H^3N + C^2NCl = H^3N,HCl + \underbrace{H^2N,C^2N}_{\text{Cyanamide.}}.$$

Again when gaseous chloride of cyanogen is passed through a solution of ethylamine or diethylamine in anhydrous ether, similar products are formed, viz., a hydrochlorate of the base, and *Cyanethylamide* or *Cyano-diethylamide:*

$$2C^4H^7N + C^2NCl = C^4H^7N,HCl + \underbrace{C^4H^6N,C^2N}_{\text{Cyanethylamide.}}.$$

and

$$2C^8H^{11}N + C^2NCl = C^8H^{11}N,HCl + \underbrace{C^8H^{10}N,C^2N}_{\text{Cyano-diethylamide.}}.$$

This last compound, cyano-diethylamide, is likewise obtained by the dry distillation of cyanethylamide. On distilling that substance in the oil-bath at 180°, cyano-diethylamide distils over, and an amber-coloured substance, $C^8H^8N^4$, which solidifies completely as it cools, remains behind:

$$\underbrace{3C^6H^6N^2}_{\text{Cyanic ethylamide.}} = \underbrace{C^{10}H^{10}N^2}_{\text{Cyano-diethylamide.}} + C^8H^8N^4.$$

Cyano-diethylamide is a limpid colourless liquid having a cyanic odour. It boils regularly and without decomposition at 190°. Does not form definite compounds with acids, but is resolved, under the influence of acids or of alkalis, into carbonic acid, ammonia, and diethylamine:

$$C^{10}H^{10}N^2 + 2KO + 4HO = 2(KO,CO^2) + NH^3 + C^8H^{11}N.$$

Methylethylamine treated with gaseous chloride of cyanogen, yields a similar product, viz., *Cyano-methylethylamide*, C^6H^8N,C^2N (Cahours & Cloez).

[These compounds may be regarded as ammonia, ethylamine, &c., in which 1 At. H is replaced by cyanogen; thus: cyanamide = N(H,H,Cy); cyanethylamide = N(H,Ac,Cy).]

g. Nitrogen-nuclei.

a. Nitrogen-nucleus. C^4NH^3.

Acetonitrile. C^4NH^3.

DUMAS (1847). *Compt. rend.* 25, 383.
DUMAS, MALAGUTI & LEBLANC. *Compt. rend.* 25, 442 *and* 474.

Cyanide of Methyl, Methylic Cyanide, Cyanformafer, Cyanmethyl, Azoture d'Acetyle, Cyanhydrate de Methylene, Cyanure de Méthyle. [Already described, VIII, 60, 61, as *Cyanide of Methyl.*]

Formation and Preparation. 1. By distilling crystallized acetate of ammonia with anhydrous phosphoric acid, digesting the distillate with a saturated aqueous chloride of calcium solution, and then distilling it over dry chloride of calcium and magnesia (Dumas).

$$NH^3,C^4H^4O^4 = C^4NH^3 + 4HO.$$

2. By distilling dry cyanide of potassium with a fixed alkaline sulphomethylate, acetonitrile is obtained, contaminated with hydrocyanic acid and formiate of ammonia, which impart to it an intolerable taste and smell, and likewise a poisonous action; from these impurities it may be freed by heating it, first over mercuric oxide, then over anhydrous phosphoric acid, the poisonous action being for the most part destroyed at the same time (Dumas, Malaguti & Leblanc):

$$C^2NK + C^2H^3KO^2,2SO^3 = C^4NH^3 + 2(KO,SO^3).$$

Properties. Thin, transparent, colourless liquid. Boils constantly at 77°. Vapour density = 1·45 (Dumas).

			Dumas.				Vol.		Density.
4 C	24	....	58·54	....	57·4	C-vapour	4	....	1·6640
N	14	....	34·14	....	34·7	N-gas	1	....	0·9706
3 H	3	....	7·32	....	7·4	H-gas	3	....	0·2079
C^4NH^3	41	....	100·00	....	99·5	Vap. of Acetonitrile	2	....	2·8425
							1	....	1·4212

May be regarded as Hydrocyanate of methylene = C^2H^2,HCy (Dumas). The compound obtained by (2) exhibits the same properties and reactions as that prepared by (1) (Dumas, Malaguti, and Leblanc).

Decompositions. 1. Boiling potash-ley forms with acetonitrile, acetate of potash and ammonia:

$$C^4NH^3 + 3HO + KO = C^4H^3KO^4 + NH^3.$$

Potassium, even at ordinary temperatures, acts violently and with evolution of heat, on acetonitrile, forming cyanide of potassium and a combustible mixture of hydrogen and carburetted hydrogen gas (Dumas). Probably thus:

$$C^4NH^3 + K = C^2NK + C^2H^2 + H.$$

according to this equation, the hydrocarbon should be methylene (VII, 246). — Nitric acid exerts no decomposing action, even at a boiling heat; neither does chromic acid (Dumas).

Combinations. Acetonitrile is miscible with water (Dumas, Malaguti & Leblanc).

β. *Nitrogen-nucleus.* C^4NCl^3.

Chloracetonitrile. C^3NCl^3.

Dumas, Malaguti & Leblanc (1847). *Compt. rend.* 25, 442.

Obtained by distilling terchloracetate of ammonia or chloracetamide with anhydrous phosphoric acid:

$$NH^3,C^4Cl^3HO^4 = C^4NCl^3 + 4HO$$

and:

$$C^4NCl^3H^2O^2 = C^4NCl^3 + 2HO.$$

Liquid of sp. gr. 1·444; boiling at 81° and yielding a diatomic vapour.

Chloracetonitrile boiled with potash yields ammonia and terchloracetate of potash:

$$C^4NCl^3 + 3HO + KO = C^4Cl^3KO^4 + NH^3.$$

Potassium acts on it with great violence (Dumas, Malaguti & Leblanc).

γ. *Nitrogen-nucleus.* C^4NXH^3.

Fulminic Acid. $C^4N^2H^2O^4 = C^4NXH^2$?

Howard. Fulminating Mercury and Fulminating Silver. *Phil. Trans.* 1800; also *Scher. J.* 5, 606; also *Gilb.* 37, 75.

Liebig. *Repert.* 12, 412; *Repert.* 15, 361; also *Ann. Chim. Phys.* 24, 298; also *Gilb.* 71, 393; also *N. Tr.* 8, 2, 123. — *Schw.* 48, 376. — *Kastn. Arch.* 6, 327; also *Ann. Chim. Phys.* 32, 316. — *Mag. Pharm.* 35, 227. — *Pogg.* 15, 564. — *Ann. Pharm.* 26, 146; 50, 429.

Gay-Lussac & Liebig. *Ann. Chim. Phys.* 25, 285; also *Schw.* 41, 179; also *Pogg.* 1, 87; also *Kastn. Arch.* 2, 58.

Pagenstecher. Fulminating Mercury. *Br. Arch.* 7, 293.

Knallsäure, Acide Fulminique.

Howard showed in 1800, that nitrate of mercury or nitrate of silver heated with alcohol and excess of nitric acid, yields a peculiar, crystalline, easily detonating precipitate, viz. *fulminating mercury* or *fulminating silver*; but the composition of these precipitates remained unknown till 1824, when it was discovered by Liebig, whose determination was afterwards confirmed by Gay-Lussac.

The rational formula of these compounds is still however the subject of many different theories, viz. the following:

The empirical formula of fulminating silver is either C^2NAgO^2 or $C^4N^2Ag^2O^4$. In the former case, it would be isomeric or metameric with cyanate of silver, from which however it differs remarkably in its properties. If fulminating silver $= C^4N^2Ag^2O^4$,—an assumption which appears not only admissible, since fulminating silver is formed from alcohol, $C^4H^6O^2$, but even necessary, inasmuch as in certain reactions of this

compound, one-half of the silver appears to be in a different state to the other,—we have still a choice between the rational formulæ proposed severally by Liebig, by Berzelius, and by Laurent & Gerhardt.

Gay-Lussac & Liebig give the formula $2AgO,Cy^2O^2$, and regard the compound as bibasic fulminate of silver. They assume in fact a bibasic fulminic acid, which, in the hypothetical anhydrous state $= C^4N^2O^3 = Cy^2O^2$, and in the hydrated state $= 2HO,C^4N^2O^2 = 2HO,Cy^2O^2$, but is unknown, even in the latter state. According to this theory, fulminating mercury is a mercuric difulminate $= 2HgO,Cy^2O^2$; acid fulminate of silver $= AgO,HO,Cy^2O^2$; fulminate of silver and potassium $= KO,AgO,Cy^2O^2$. This view is supported by the fact that in many reactions of fulminating silver, hydrocyanic acid, *i. e.* a cyanogen-compound, is formed.

Gerhardt (*Précis*, 2, 445) and Laurent regard fulminating silver as $C^4N(NO^4)Ag^2 = C^4NXAg^2$, that is, as a secondary nucleus derived from ethylene, just as cyanide of silver, C^2NAg, is a secondary nucleus derived from methylene. As cyanide of silver, C^2NAg, is derived from a nucleus C^2NH (hydrocyanic acid) containing H, so doubtless may fulminating silver be derived from the nucleus C^4NXH^2, a compound not at present known, but identical with Liebig's fulminic acid $= 2HO,Cy^2O^2$. According to this view, fulminating mercury $= C^4NXHg^2$; the so-called acid fulminate of silver $= C^4NXHAg$; and fulminate of silver and potassium $= C^4NXKAg$. In favour of this view it may be urged, that the compounds in question are produced by nitric acid, which so readily introduces hyponitric acid $= NO^4 = X$ into the decomposed compound in place of hydrogen, — and that this substitution affords the most satisfactory explanation of the detonating properties of these compounds, wherein they differ from the cyanates and agree with the majority of nitro-compounds.

Berzelius (*Berz. Jahresber.* 24, 87) supposes that these fulminating compounds contain a metallic nitride. Thus, the acid fulminate of silver obtained by Gay-Lussac & Liebig $= HO,AgN,C^4NO^3$; by separation of 1HO, this compound is converted into AgO,AgN,C^4NO^3. As the 2 At. silver are here supposed to be in different states (the one being associated with N as a copula in the acid, the other with O in the bases) we have an explanation of the fact, that in many decompositions of fulminating silver, only the latter atom is separated. The same view explains why the so-called fulminate of silver and potassium, KO,AgN,C^4NO^3, detonates as strongly as fulminate of silver AgO,AgN,C^4NO^3; the quantity of AgN, whose decomposition produces the detonation, being in fact the same in both cases. If the detonation were caused, as Gay-Lussac and Liebig suppose, by the oxygen of the silver-oxide or mercuric oxide, passing over readily and with evolution of light and heat, to the carbon, then $KO,AgO,C^4N^2O^3$, ought to detonate less strongly than $2AgO,C^4N^2O^3$. — This circumstance is equally in favour of Gerhardt & Laurent's theory.

For Kühn's theory, *vid.* Kühn (*Schw.* 61, 503) and Liebig (*Mag. Pharm.* 35, 227).

The following description of these compounds is based upon Gerhardt & Laurent's view; but the old names have been for the most part retained.

Fulminating Zinc or Neutral Fulminate of Zinc.

$C^4N^2Zn^2O^4 = C^4HXZn^2$.

EDM. DAVY. *Transact. of the Dublin Soc.* 1829; abstr. *Berz. Jahresber.* 12, 95 & 120. — Fehling. *Ann. Pharm.* 27, 130.

Liebig showed that when zinc is boiled with fulminating mercury and water, mercury is separated, and a yellow liquid produced which on cooling deposits yellowish, slightly detonating crystals. E. Davy in 1829, examined more minutely the compound thence resulting.

1 pt. of fulminating mercury is placed under water in contact with 2 pts. of zinc-filings, and the whole frequently shaken, till all the mercury is precipitated and an amalgam formed, after which the filtrate is left to evaporate spontaneously.

Transparent, colourless, rhombic tables, which are tasteless; detonate very strongly at 195°, or by percussion or by contact with oil of vitriol; are insoluble in water; but dissolve in aqueous alkalis. — If the filtrate be evaporated, not in the cold, but at a gentle heat, there remains a deep yellow crust together with yellow needles, which do not detonate by contact with oil of vitriol, but when heated, detonate as readily, but not so violently, as the first-mentioned crystals; this latter product is insoluble in cold water and alcohol, but dissolves sparingly in boiling water and very readily in ammonia. — An aqueous solution of fulminate of zinc poured into a bottle filled with chlorine gas, yields a volatile, strongly smelling oil, which has a sweet and bitter taste, does not detonate, is insoluble in water, and reddens litmus after some time only. (Davy) [C^4NXCl^2?].

The liquid filtered from the zinc-amalgam, and containing the fulminating zinc, yields with nitrate of silver a white precipitate soluble in hot water, and detonating violently when heated. With hydrochloric acid, it gives out a strong odour of hydrocyanic and cyanic acid. It decomposes, even during evaporation over the water-bath, yielding a yellow powder, partially soluble in water. The soluble portion of this powder yields, with silver-salts, a white non-fulminating powder, while the insoluble part gives off ammonia, and leaves white oxide of zinc when heated, and dissolves in acids with evolution of hydrocyanic acid (Fehling).

Fulminate of Zinc and Hydrogen, or Acid Fulminate of Zinc.

The aqueous solution of fulminating zinc, recently prepared by the action of zinc on fulminating mercury, is precipitated by excess of baryta-water, which separates a large quantity of oxide of zinc; the excess of baryta removed by a stream of carbonic acid; the filtrate, which contains fulminate of zinc and barium, and throws down fulminate of silver from a solution of the nitrate, treated with the exact quantity of sulphuric acid required to remove the barium; and the liquid filtered. The filtrate contains a large quantity of zinc (Fehling).

The reaction is as follows:

$$C^4NXHg^2 + Zn^2 = C^4NXZn^2 + Hg^2;$$

then:

$$C^4NXZn^2 + BaO = C^4NXZnBa + ZnO;$$

finally:

$$C^4NXZnBa + HO,SO^3 = C^4NXZnH + BaO,SO^3.$$

The same process was previously employed by E. Davy, who however supposed that the baryta threw down all the zinc, and that the liquid remaining after precipitation of the baryta by sulphuric acid was pure fulminic acid = C^4NXH^2.

The filtrate has a powerful odour, like that of hydrocyanic acid; tastes agreeably sweet at first, but afterwards pungent and astringent; it volatilizes when exposed to the air [?]. When kept in a bottle, it gradually loses its odour, becomes yellow, and deposits a yellow powder, but still forms an explosive yellow precipitate with nitrate of silver (E. Davy).

By saturating the filtrate with different bases, the double salts of fulminating zinc are obtained, in which the 1 At. of zinc [hydrogen?] is replaced by 1 At. of another metal or of ammonium (they were regarded by Davy as pure fulminates). These salts detonate, according to Davy, between 175° and 230°; most of them are soluble in water, and have a sweetish rough taste; their solutions precipitate nitrate of silver.

Ammonium-salt. — The solution evaporated to a syrup, solidifies in the crystalline form. The salt has an alkaline reaction, deflagrates with a yellow flame when heated, and on exposure to the air, becomes moist, but does not decompose.

Potassium-salt. — Transparent, colourless, rhombic prisms, which have an alkaline reaction, and a sweetish rough taste; explode violently, with a pale red flame, by heat, percussion, or contact with oil of vitriol; deliquesce in the air; but are insoluble in alcohol (E. Davy).

Sodium-salt. — Efflorescent, oblique rhombic prisms with dihedral summits. Detonates like the potassium-salt.

Barium-salt. — Crystallizes from the syrupy solution in flat, transparent four-sided prisms, which are alkaline; explode like the potassium-salt; turn yellow when exposed to the air; and are soluble in alcohol (E. Davy).

Strontium-salt. — Small, transparent needles.

Calcium-salt. —Very small, alkaline, detonating crystals, which turn yellow when heated; become moist when exposed to the air; and are sparingly soluble in water.

Magnesium-salt. — Long, flat, four-sided prisms, which are opaque; neutral; explode by heat or percussion, but not by contact with oil of vitriol; and dissolve readily in water and in alcohol.

Aluminum-salt. — Yellow, indistinctly crystalline, neutral, slightly detonating, easily soluble.

Chromic Salt. — Small, yellow-green, detonating crystals, easily soluble in water.

become covered with mercury; the hot filtered liquid is pale green, and deposits on cooling a pale green powder which explodes with a green flame, but contains only a small quantity of copper, and therefore gives but a faint blue colour with ammonia; a true fulminate of copper has not yet been obtained (Pagenstecher).

¶ *Fulminate of Copper and Ammonium*, $C^4NXCu(NH^4)$. — Formed by mixing a solution of fulminate of copper (obtained by leaving fulminate of silver for some time in contact with metallic copper and a large quantity of water) with a large excess of ammonia, 1 At. copper being then replaced by 1 At. ammonium. When a stream of sulphuretted hydrogen is passed through the solution of this salt, the copper is completely precipitated, and the filtered solution is founded to contain hydrosulphocyanic acid and urea:

$$C^4NCu(NH^4)O^4 + 3HS = CuS + 2HO + C^2NHS^2 + C^2N^2H^4O^2.$$

The formation of urea from this salt is in favour of Gay-Lussac & Liebig's view of the relation between the fulminates and cyanates (Gladstone, *Ann. Pharm.* 66, 1; *comp* VII, 362). ¶.

Fulminate of Copper and Potassium. — By digesting fulminate of silver and potassium with copper, the silver is precipitated and a liquid obtained, which is neither precipitated by potash nor turned blue by ammonia, unless it be previously mixed with hydrochloric acid (Liebig).

Fulminating Mercury, Howard's Fulminating Mercury, or Mercuric Fulminate.

Formation. When mercury or mercuric oxide is heated with strong nitric acid and alcohol, the liquid boils up and gives off a white cloudy vapour, called *ethereal nitrous gas* (VIII, 217), containing mercury besides the products there mentioned; and as this vapour diminishes, the fulminating mercury separates out in crystals which are still impure (Howard). — 2. Fulminating silver boiled with mercury and water is converted into fulminating mercury (Liebig). — 3. An aqueous solution of fulminating zinc, added to aqueous protochloride of mercury, throws down fulminating mercury (E. Davy).

Preparation. A solution of 1 pt. mercury in 7·5 pts. hot nitric acid of sp. gr. 1·30 is mixed with 10 pts. of alcohol of sp. gr. 0·85; the mixture heated till it begins to froth; and the crystals which form on cooling, collected on a filter, washed with cold water, and dried. In this manner, from 1·20 to 1·32 pts. of fulminating mercury are obtained (Howard). — On adding the alcohol, mercurous nitrate is precipitated in the form of a white powder, which redissolves on heating; but the liquid immediately afterwards assumes a grey colour, from separation of 30 to 40 p.c. of the mercury used; it then turns yellow, giving off the thick white mercurial vapour, and deposits greyish white crystals of fulminating mercury, the quantity of which increases as the liquid cools; the mother-liquid yields on evaporation a small quantity of fulminating silver, whilst mercuric oxalate remains in it, being held in solution by the nitric acid (Liebig). — The liquid must be boiled for two minutes

longer after the addition of the alcohol; if it be heated, either for too short or too long a time, the preparation fails (Fourcroy, Thénard).

Wright (*Gilb.* 76, 74) dissolves 1 pt. of mercury in 4 pts. of boiling nitric acid; adds 3·5 pts. of alcohol when the liquid is perfectly cold; promotes the ebullition, if necessary, by heating the liquid for a short time, allowing the boiling to go on till the white fume which rises up turns reddish; then precipitates the fulminating mercury by cold water, and washes it with water by decantation. — Cremascoli (*Ann. Pharm.* 10, 88) dissolves 1 pt. of mercury in 12 pts. of nitric acid of 34° Bm.; adds 8 pts. of alcohol of 36° Bm. after the liquid has cooled to 12·5°; heats the flask in boiling water for two or three minutes, till thick white fumes begin to form (the action being otherwise but slight); sets it in a cool place; collects the resulting crystals on a filter; washes them with a small quantity of water; and dries them between paper in the dark. The product amounts to 1·25 pt. — Guthrie takes 13 pts. nitric acid of sp. gr. 1·34 and 8 pts. alcohol to 1 pt. of mercury.

In the preparation of fulminating mercury on the large scale for percussion caps, 1½ lb. of mercury is dissolved at a gentle heat in 18 lbs. of pure nitric acid of 36° Bm. contained in a large glass flask; then gradually mixed with 8 to 10 litres of alcohol, and heated if necessary till it begins to boil up; then after the ebullition has ceased, and the liquid has completely cooled, the liquid is poured off, and the fulminating mercury left to drain on linen filters in glass funnels, washed with a little pure water, and dried (Chevallier, *J. des connaiss. usuelles;* also *Ann. Pharm.* 23, 167).

Purification. The fulminating mercury is dissolved in boiling water; the yellow solution filtered from the metallic mercury; and the yellow needles which crystallize out on cooling, purified by again dissolving them in hot water and crystallizing (Liebig).

Properties. White needles, having a silky lustre, very soft to the touch, and of sweetish metallic taste (Liebig):

	Probable Calculation.			Howard.	Liebig.
4 C	24	....	8·45		
2 N	28	....	9·86		
2 Hg	200	....	70·42	..... 64·72	..... 56·9
4 O	32	....	11·27		
C^4NXHg^2	284	....	100·00		

Crystallized fulminating mercury probably contains water of crystallization; the presence of this water would explain the deficiency in the mercury found by analysis. — Liebig and Berzelius regard fulminating mercury as mercurous fulminate = $C^4N^2Hg^4O^4 = 2Hg^2O,Cy^2O^2$; but according to this formula, it should contain 82·6 p.c. mercury. Moreover potash separates from it not mercurous but mercuric oxide.

Decompositions. 1. Fulminating mercury explodes when heated to 187° (to 145°, according to Thénard, *Ann. Chim. Phys.* 44, 181), by contact with burning tinder, by the spark from flint and steel (but according to Schmidt, *Schw.* 41, 73, only when quite dry), by the electric spark, by friction or percussion, and by contact with oil of vitriol (Howard). The explosion is accompanied by a reddish light, and produces a black spot having the metallic lustre (Liebig). The detonation produced by heat, by burning tinder, or by flint and steel, is much less violent than that

produced by friction, percussion, or the electric spark, probably because in the latter cases, the explosion of the whole quantity takes place more simultaneously. 10 grains of fulminating mercury yield by explosion, in addition to water and metallic mercury, only 4 English cubic inches of a mixture of carbonic acid and nitrogen gases. 34 grains of fulminating mercury are sufficient to burst strong fire-arms; smaller quantities propel the ball, but with much less force than gunpowder. — On the very powerful action of fulminating mercury in its immediate neighbourhood, and slight effect even at small distances, vid. *Schw.* 29, 88.— On the variation in the facility with which fulminating mercury takes fire, and, on its application to percussion-caps, vid. Aubert, Pelissier & Gay-Lussac (*Ann. Chim. Phys.* 42, 8).

2. Heated nitric acid decomposes fulminating mercury, yielding carbonic acid, acetic acid, and mercuric nitrate (Howard).—3. Moderately dilute sulphuric acid decomposes it without detonation, but with rise of temperature and evolution of gas (Howard). In this reaction, 84 p.c. of a white, non-detonating powder is separated, apparently a mixture of metallic mercury with mercurous oxalate (mercurous sulphate, according to Berthollet), whilst also a small quantity of mercury appears to remain dissolved in the liquid containing the sulphuric acid. 100 grains of fulminating mercury distilled with a mixture of water and oil of vitriol in equal parts, yield from 28 to 31 English cubic inches of a gaseous mixture which coats the mercury in the trough with a black powder, and contains, besides carbonic acid, from 5 to 7 Engl. cub. in. of a gas which burns with a greenish blue flame, does not explode by the electric spark when mixed with hydrogen, and is not absorbed by water (Howard).

4. Aqueous hydrochloric acid decomposes fulminating mercury, without any considerable evolution of gas, forming mercuric chloride and mercurous oxalate (Howard). It produces mercuric and mercurous chloride, together with sal-ammoniac (Thénard). It produces a large quantity of hydrocyanic acid (Ittner). — 5. Sulphuretted hydrogen converts fulminating mercury immersed in aqueous ammonia, into sulphide of mercury and hydrosulphocyanic acid (Pagenstecher):

$$[C^4N^2Hg^2O^4 + 6HS = 2HgS + 2C^2NHS^2 + 4HO\ ?]$$

6. Boiling potash-solution separates a large quantity of mercuric oxide, without evolution of ammonia, and yields a filtrate, which, as it cools, deposits yellow detonating flakes and needles, probably consisting of potassio-mercuric fulminate [$C^4N^2HgKO^4$?], and forms with nitric acid a white precipitate, which detonates strongly by percussion. Baryta, strontia, and lime behave like potash (Liebig). — Potash-ley exerts no action in the cold; when hot, it separates mercuric oxide, but the filtrate yields by evaporation, not a dentonating salt, but only carbonate of potash. Cold baryta-water likewise exerts no action; hot baryta dissolves a small quantity of fulminating mercury, leaving the rest unaltered; and the liquid, if afterwards exposed to the air, deposits all the baryta in the form of carbonate, so that sulphuric acid no longer forms any precipitate in it; sulphuretted hydrogen, on the other hand, forms a brown precipitate, as with the solution of fulminating mercury in pure water (Pagenstecher). — Fulminating mercury mixed with a small quantity of strong potash, thickens in the course of an hour or two; if small quantities of potash be then added, till, after about 48 hours, the mixture no longer becomes pasty, it is found to have increased to about four times the original volume of the fulminating mercury. A sample of the mixture taken out at the end of the first day, wrapped up in cloth, and strongly

pressed in a vice, leaves a mass, which is sometimes hot and detonates spontaneously after a while; if this does not take place, it exhibits, after drying at 100°, an explosive power equal to that of fulminating silver. In four days, however, the mixture loses its explosive power, and when heated after drying, merely exhibits a slight deflagration. Carbonate of potash, soda and ammonia, and lime-water, first heighten the explosive power of fulminating mercury, and then destroy it (Guthrie, *Sill. Am. J.* 21, 289 and 293).

7. A solution of fulminating mercury in warm aqueous ammonia deposits, on cooling, yellow, strongly detonating, granular crystals; but if the solution be boiled for some time, it deposits, on cooling, a yellowish white, non-detonating-powder (Liebig). Fulminating mercury dissolves abundantly in ammonia, without separation of oxide; the solution, when exposed to the air, gives off ammonia, and becomes covered with a crystalline crust of unaltered fulminating mercury, which renews itself as often as it is broken (Pagenstecher).

8. Finely divided zinc, copper, or silver (the last in contact with platinum-foil) boiled in water with fulminating mercury, decomposes that compound, yielding metallic mercury and fulminate of zinc, copper or silver (Liebig). Respecting zinc and copper, vid. pp. 297, 299. — By agitating iron filings with fulminating mercury and water, mercury separates after a few hours, and a yellow liquid is obtained, which yields detonating precipitates with lead and silver salts, and with potash, a dark green precipitate, which soon turns brown. The yellow liquid, when boiled, first becomes wine-red, then black and blue, and yields a precipitate of the same colour, which dries up to a brown, non-detonating mass. The yellow liquid, when recently prepared, assumes a deep red colour on the addition of an acid, loses its colour after a few hours, and then smells, first of fulminic [?], and afterwards of hydrocyanic acid (E. Davy). — A pasty mixture of fulminating mercury with pulverized iron and water, moderately warmed, becomes strongly heated, and dries up almost completely to a red-brown mass; this, when mixed with lukewarm water and filtered, yields a filtrate which, on evaporation, leaves a small saline residue containing ammonia; and on the filter there remains a black-brown residue which contains globules of mercury; yields prussian blue with hydrochloric acid; and when heated after drying, burns with bright sparkling, but without detonation (Pagenstecher).

Fulminating mercury dissolves very sparingly in cold water, more readily in hot water (Howard). It dissolves slightly in aqueous ammonia (Liebig, Pagenstecher).

Respecting the double fulminates of mercury and potassium, barium, strontium, and calcium, vid. p. 302, 6.

Mercurous nitrate forms with fulminating zinc, an iron-grey precipitate, which detonates slightly by heat or by percussion (E. Davy).

Fulminating Silver. Howard's (Brugnatelli's) Fulminating Silver, or Neutral Fulminate of Silver.

Formation. 1. By heating aqueous nitrate of silver with strong nitric acid and alcohol, the same phenomena and products appearing as in the formation of fulminating mercury (p. 300). Neutral nitrate of silver does not yield fulminating silver when boiled with alcohol; the formation of that compound requires the presence of nitrous acid, inasmuch as

cyanogen is thereby produced; when nitrous acid vapour is
an alcoholic solution of nitrate of silver, fulminating sil
separates in large needles, without ebullition of the liquid (L
Pharm. 5, 287):

$$C^4H^6O^2 + 2(AgO,NO^5) + 2NO^3 = C^4N^2Ag^2O^4 + 6HO + 2$$

2. Fulminating mercury is converted into fulminating silve
with water, pulverized silver, and platinum-filings (Liebig).

Preparation. Nitrate of silver is heated with alcohol
nitric acid till the liquid begins to boil up; and the crystals
ing silver which form during the ebullition and as the liqui
collected on a filter, washed with cold water, and dried either
or at most at the heat of the water-bath.

The preparation of fulminating silver requires the great
Capacious vessels must be used, so that the liquid may not b
in that case the salt might dry on the outside and then explod
must be removed to a distance, lest the vapours should take fi
mixture must be stirred with wooden rods, not with glass r
hard bodies. Contact with hard bodies must especially be a
the preparation is dry. Paper shovels must be used to transf
must be kept in vessels of paper or paste-board, not of glas
vessels must be loosely covered, as an explosion might ari
friction of the stopper, or from pressing the cover of the b
(*Gilb.* 37, 64).

Howard and Cruickshank dissolve 1 pt. of silver in a
24 pts. water and 24 pts. of the strongest nitric acid, ad
alcohol, and obtain 1·5 pt. of fulminating silver. — Brugnatell
1, 665), pours 5 pts. alcohol, and then 5 pts. fuming nitric a
of pulverized lunar caustic, and at the proper time cools th
which boils up and deposits fulminating silver, with water, to
fulminating silver from being decomposed. — Accum recomme
of fuming nitric acid, and 7 pts. of alcohol to 1 pt. of nitrate o
Descotils (*Ann. Chim.* 62, 198, also *Gilb.* 28, 44), adds
to the nitric acid as the silver dissolves in it; as however
interferes with the solution of the silver, the product is,
to Liebig, greatly diminished thereby. — Wagenmann (*Gilb*
mixes a solution of 1 pt. silver in 8 pts. nitric acid of s
heated to 50° or 60°, with 8 pts. alcohol of sp. gr. 0·85; heats
again to 50° or 60°; and adds 4 pts. of fuming nitric acid, w
foaming and formation of fulminating silver, in quantity at
to $\frac{3}{4}$ of the silver used. — The quantity of alcohol here recor
too small; and the liquid becomes too hot, whereby the fulmin
is decomposed (Liebig). — Gay-Lussac & Liebig dissolve 1 pt.
20 pts. nitric acid of 40° Bm.; add to the solution 27 pts. of 8
alcohol, heat the mixture till it boils up; remove the liqui
becoming turbid, from the fire; mix it, in order to moderate th
with another 27 pts. of alcohol; and obtain, after the liquid
pletely cooled, about 1 pt. of fulminating silver. The moth
fulminating silver is green if the silver contains copper,
evaporated, deposits all the copper in the form of oxalate;
remains a liquid containing silver, which, when further evapor
a red salt, easily soluble in water (Liebig).

Properties. Small, white, opaque shining needles, havin

bitterish metallic taste (Descotils, Liebig). According to Pajot-la-Fôret, fulminating silver kills cats with violent convulsions; according to Ittner, 5 grains of it are sufficient, and produce narcotic symptoms. When properly washed, it is neutral and has no caustic action (Liebig):

	Crystallized.			Gay-Lussac & Liebig.	Descotils.
4 C	24	....	8·00	..... 7·92	
2 N	28	....	9·33	..... 9·24	
2 Ag	216	....	72·00	..... 72·19	 71
4 O	32	....	10·67	..... 10·65	
C^4NXAg^2	300	....	100·00	..... 100·00	

Or:

				Gay-Lussac & Liebig.
2 Cy	52	....	17·33	..... 17·16
2 AgO	232	....	77·34	..... 77·53
2 O	16	....	5·33	..... 5·31
$2AgO,Cy^2O^2$	300	....	100·00	..... 100·00

Decompositions. 1. Fulminating silver gradually blackens in white and in blue light, giving off carbonic acid, nitrogen and aqueous vapour [?] and leaving a black suboxide [?], mixed with a small quantity of the undecomposed compound (Liebig). — 2. It explodes much more violently than fulminating mercury, by heat, by the electric spark, by friction or percussion, or by contact with oil of vitriol. — A heat of 100° to 130° is not sufficient to induce the explosion of dry fulminating silver (Liebig). — It does not explode by mere pressure, unless the pressure be very strong (Descotils). — In the moist state, it requires a much harder blow to explode it than when dry, but it will sometimes explode, even under water, by friction with a glass rod (Figuier, *Ann. Chim.* 63, 104; Liebig). — It explodes with peculiar readiness when rubbed with glass-dust or quartz-sand; also when dry, with the edge of a playing card (Figuier). On the other hand, it may be rubbed to powder in a porcelain mortar with a cork or with the finger (Liebig). — Fulminating silver well washed and then exposed to the sun till it is dry, explodes on the slightest touch (Trommsdorff, *Gilb.* 31, 112). — Oil of vitriol causes moist fulminating silver to detonate as strongly as the dry compound (Schmidt, *Schw.* 41, 72). — The light accompanying the explosion, which is most easily seen in the dark, is blue reddish white; it is succeeded by a grey vapour having a peculiar electrical odour. Gunpowder mixed with fulminating silver is not ignited by the explosion, but merely scattered about (Liebig). — When fulminating silver is exploded by oil of vitriol or by percussion (in the latter case, provided it be moist), the odour of hydrocyanic acid is perceptible (Ittner, Dobereiner.) — Fulminating silver, mixed with 20 times its weight of finely pulverized sulphate of potash, gradually decomposes when heated in a tube, yielding 2 vol. carbonic acid to 1 vol. nitrogen (also carbonate of ammonia, if moisture be present), and doubtless leaves dicyanide of silver, C^2NAg^2 [now called paracyanide of silver, VIII, 27]: for the residue mixed with cupric oxide and ignited, again yields the same gaseous mixture, in about the same quantity and the same proportions as by the first ignition (Gay-Lussac & Liebig). Therefore, in the first instance:

$$C^4N^2Ag^2O^4 = C^2NAg^2 + 2CO^2 + N.$$

afterwards, when ignited with cupric oxide:

$$C^2NAg^2 + 4O = Ag^2 + 2CO^2 + N.$$

A mixture of 1 pt. fulminating silver and 40 pts. cupric oxide when heated, immediately gives off, without detonation, the whole of the carbonic acid and nitrogen gases in the proportion by volume of 2 to 1 (Gay-Lussac & Liebig).

3. Fulminating silver thrown into a bottle filled with chlorine explodes before it reaches the bottom, and therefore does not break the bottle (E. Davy). — Fulminating silver well moistened with water and exposed to a current of chlorine gas, absorbs a large quanity of the gas, turns yellow, and is finally converted, without any formation of carbonic or chloric acid, into chloride of silver, and a yellow oil, heavier than water, having a pungent odour, attacking the eyes strongly, and having a sharp burning taste which almost paralyzes the tongue. If the mixture be agitated with water and distilled, gas is given off before the water begins to boil, and a colourless oil passes over, having a somewhat less powerful odour. This oil gives off gas under water; is insoluble in aqueous alkalis, but dissolves in alcohol; and, if mixed in this solution, first with potash, then with a ferric salt, and then with an acid, exhibits a green colour. This oil is therefore related to the oil of chloride of cyanogen (Liebig, *Pogg.* 15, 564). [May it not be C^4NXCl^2, as indicated by the following equation?

$$C^4N^2Ag^2O^4 + 4Cl = C^4N^2Cl^2O^4 + 2AgCl.]$$

4. Nitric acid boiled for some time with fulminating silver, decomposes it, forming nitrate of ammonia and nitrate of silver (Descotils.) — 5. Dilute sulphuric or oxalic acid decomposes fulminating silver without effervescence, forming hydrocyanic acid and ammonia (Gay-Lussac & Liebig).

6. Aqueous hydrochloric acid immediately converts all the silver of fulminating silver into chloride of silver, with evolution of the odour of hydrocyanic acid (Descotils). — Besides chloride of silver and hydrocyanic acid, a trace of ammonia is obtained, but no oxalic acid (Ittner). — By a comparatively small quantity of hydrochloric acid, the fulminating silver is converted into chloride of silver and acid fulminate of silver, AgO,HO,Cy^2O^2 [$=C^4NXAgH$]; but on adding hydrochloric acid till the filtrate is no longer clouded by it, the acid fulminate is converted into chloride of silver, hydrocyanic acid, and a peculiar chlorinated acid; neither ammonia nor carbonic acid is formed in this reaction (Gay-Lussac & Liebig). To judge by the odour, a large quantity of hydrocyanic acid is formed; but on passing hydrogen gas through a mixture of fulminating silver and hydrochloric acid, then over marble, and lastly into solution of nitrate of silver, no precipitate is formed (Gay-Lussac & Liebig. [Hence there is perhaps formed an acid smelling like hydrocyanic acid, but not identical with it.]

The *chlorinated acid* contains carbon, nitrogen, chlorine, and perhaps also hydrogen. The chlorine contained in it appears to amount to 2·5 times as much as that which is contained in the chloride of silver produced. It tastes pungent and sweetish, reddens litmus strongly, and does not precipitate nitrate of silver. It decomposes when exposed to the air for some hours, more quickly when heated, yielding ammonia, which neutralizes the still-undecomposed portion of the acid. After neutralization with potash, whereby it first acquires a rose-red, then a

yellow colour, or after it has been saturated with ammonia by spontaneous decomposition, it colours ferric salts deep red. The acid saturated with potash gives off ammonia when evaporated, and leaves a residue which effervesces strongly with acids, and whose aqueous solution precipitates nitrate of silver (Gay-Lussac & Liebig).

7. Aqueous hydriodic acid decomposes fulminating silver in a similar manner, yielding iodide of silver and an iodurетted acid, analogous to the chlorinated acid, but forming a deep red precipitate with sesquichloride of iron, without being first neutralized. In this decomposition by hydriodic acid also, no odour of hydrocyanic acid is perceptible (Gay-Lussac & Liebig). — Hydrofluoric acid does not decompose fulminating silver (Gay-Lussac & Liebig).

8. A small quantity of aqueous sulphuretted hydrogen decomposes fulminating silver, forming sulphide of silver and cyanic acid; a larger quantity forms sulphide of silver and hydrosulphocyanic acid:

$$[C^4N^2Ag^2O^4 + 2HS = 2C^2NHO^2 + 2AgS;$$

and

$$C^4N^2Ag^2O^4 + 6HS = 2C^2NHS^2 + 2AgS + 4HO.$$

Or, if we suppose that the cyanic acid formed at first, is converted by excess of sulphuretted hydrogen into hydrosulphocyanic acid:

$$C^2NHO^2 + 4HS = 2C^2NHS^2 + 4HO.$$

Part of the cyanic acid is resolved into carbonic acid and ammonia, which latter remains combined with the hydrosulphocyanic acid. Such at all events is the explanation which I venture to give of the following experiments of Gay-Lussac & Liebig, although these chemists regard the acid which is formed as different from hydrosulphocyanic acid.]

When fulminating silver is suspended in water, the liquid briskly agitated, and sulphuretted hydrogen passed through it in quantity not sufficient for complete decomposition, the liquid emits a pungent odour like that of cyanic acid, and forms fumes when a stopper dipped in ammonia is held over it. But when all the fulminate of silver is decomposed, the liquid becomes clear and loses all its odour. If it be then filtered from the sulphide of silver, it exhibits the following properties: It tastes harsh and reddens litmus; gives off ammonia when treated with potash; throws down sulphate of baryta from baryta-salts after boiling with nitric acid; colours ferric salts dark red; and forms a copious yellow precipitate with nitrate of silver [sulphocyanide of silver is white.] When exposed for some time to the air, it deposits a yellow powder, acquires the odour of hydrocyanic acid, and finally leaves deliquescent sulphocyanide of ammonium (Liebig, *Kastn. Arch.* 6, 327). — [It is true that Gay-Lussac & Liebig found in the sulphuretted acid obtained from 1 At. fulminating silver, only a little more than 2 At. sulphur, although the 2 At. hydrosulphocyanic acid, which 1 At. fulminating silver should according to the above equation produce, must contain 4 At. sulphur; but as part of the cyanic acid formed at the commencement is always converted into carbonate of ammonia, it is not possible that 2 At. hydrosulphocyanic should be produced.]

9. Aqueous solutions of alkaline sulphides, *e. g.* protosulphide of barium, acting in insufficient quantity, decompose cyanide of silver, yielding fulminate of silver and the alkali-metal, and sulphide of silver (Liebig):

$$C^4N^2Ag^2O^4 + BaS = C^4N^2AgBaO^4 + AgS.$$

With a larger proportion of the metallic sulphide, an alkaline fulminate ($C^4N^2K^2O^4$) appears to be formed at ordinary temperatures, and with the aid of heat, a compound of the alkali with a sulphuretted acid different from hydrosulphocyanic acid. — If fulminating silver be treated with exactly so much aqueous protosulphide of potassium (or of ammonium), that the liquid shall neither be clouded by hydrochloric acid nor blackened by nitrate of silver, the liquid filtered from the sulphide of silver is found to be perfectly neutral, tastes exactly like cyanate of potash, and when added to a solution of nitrate of silver, forms a precipitate of fulminating silver, which, if the liquid still contains sulphide of potassium, is blackened by admixture of sulphide of silver. On evaporating the filtrate, the alkaline fulminate is decomposed (Liebig, *Pogg.* 15, 566). — If to fulminating silver suspended in boiling water, aqueous protosulphide of barium be added as long as sulphide of silver continues to form, a yellow alkaline filtrate is obtained, from which, however, carbonic acid throws down only a very small quantity of carbonate of baryta. This yellow barytic filtrate does not give off sulphuretted hydrogen when treated with acids. When evaporated, it leaves a yellow residue, which at 100°, as soon as the last trace of moisture is expelled, changes to a grey mass, from which lime eliminates ammonia, and water extracts sulphocyanide of barium, leaving a residue of carbonate of baryta; the grey mass heated in a tube, melts, gives off carbonate of ammonia which sublimes, then cyanogen, and leaves sulphide of barium. Dilute sulphuric acid separates from the undecomposed baryta-salt, an easily decomposible acid. — With nitrate of silver, the recently prepared yellow barytic filtrate forms a yellow precipitate, which when washed and then heated with water to 100°, gives off carbonate of ammonia, and is converted into sulphide of silver (Liebig, *Kastn. Arch.* 6, 330).

10. Aqueous solutions of the fixed alkalis, as also magnesia, boiled with fulminating silver, gradually separate not quite half the silver, as a black oxide; a solution of fulminate of silver and potassium, sodium, barium, strontium, calcium, or magnesium being at the same time formed (Gay Lussac & Liebig):

$$C^4N^2Ag^2O^4 + KO = C^4N^2AgKO^4 + AgO.$$

100 pts. of fulminating silver, boiled even for a considerable time with excess of potash, do not yield more than 31·45 pts. of oxide of silver (Liebig). Calculation requires 38·67 pts. — 300 : 116 = 100 : 38·67. Hence part of the fulminating silver appears to remain undecomposed.

11. Aqueous solutions of the alkaline chlorides, even when added in excess, precipitate only half the silver in the form of chloride, and form fulminate of silver and potassium, &c. (Gay-Lussac & Liebig):

$$C^4N^2Ag^2O^4 + KCl = C^4N^2AgKO^4 + AgCl.$$

In this manner, 100 pts. of fulminating silver decomposed by a slight excess of chloride of potassium, yield 53·38 pts. of chloride of silver, and a solution which, when decomposed by hydrochloric acid, likewise yields 53·73 pts. of chloride of silver. Hence the two atoms of silver in the fulminate are in different states, since only one of them is precipitated as chloride of silver by metallic chlorides (Gay-Lussac & Liebig).

12. Copper or mercury boiled with fulminating silver and water ultimately separates all the silver in the metallic state, forming fulminate of copper or fulminate of mercury (Liebig). — When the boiling with mercury is continued for a short time only, fulminate of silver and

mercury is formed = $C^4N^2AgHgO^4$ (Liebig). — Zinc, even when boiled for several days with fulminating silver, separates only half the silver, so that fulminate of silver and zinc is formed (Liebig, *Schw.* 48, 308). — When fulminating silver is boiled with water and iron filings, a red-brown filtrate is obtained, which when evaporated, yields reddish, laminated crystals of fulminate of iron (Liebig, *Ann. Chim. Phys.* 24, 308).

Combinations. Fulminating silver is very sparingly soluble in cold *Water*, but dissolves in 36 pts. of boiling water, from which it separates again on cooling (Gay-Lussac & Liebig). — It dissolves more abundantly in aqueous *Ammonia*, which, when evaporated at ordinary temperatures, leaves it unaltered (Descotils).

Fulminate of Silver and Hydrogen, or *Acid Fulminate of Silver.* $C^4NXAgH = AgO,HO,Cy^2O^2$. — Precipitated in the form of a white powder on mixing the aqueous solution of a fulminate of silver and an alkali-metal, with nitric acid not in excess:

$$C^4N^2AgKO^4 + HO + NO^5 = C^4N^2AgHO^4 + KO,NO^5.$$

Dissolves readily in boiling water, crystallizing out on cooling; redden litmus. By boiling with silver-oxide, it is converted into fulminate o silver, and by boiling with mercuric oxide, into fulminate of silver and mercury (Liebig, *Ann. Chim. Phys.* 24, 302).

Fulminate of Silver and Ammonium. $C^4NXAgAm = NH^4O,AgO,Cy^2O^2$. — From a solution of fulminate of silver in hot aqueous ammonia, this salt crystallizes on cooling in white, shining, crystalline grains having a pungent metallic taste, while argentate of ammonia remains in solution. Detonates with three times the force of fulminating silver, and with extreme facility, even under the liquid, when touched with a glass rod; if, however, the liquid contains excess of ammonia, the explosion does not extend throughout the mass. Dissolves very sparingly in water (Liebig, *Ann. Chim. Phys.* 24, 316).

Fulminate of Silver and *Potassium.* $C^4NXAgK = KO,AgO,Cy^2O^2$. — 300 pts. (1 At.) fulminating silver are decomposed by not quite 74·6 pts. (1 At.) chloride of potassium dissolved in water,—or water in which fulminating silver is suspended is kept in a state of ebullition, and aqueous chloride of potassium added as long as it occasions turbidity, but no longer; the liquid is then decanted from the chloride of silver, and cooled till it crystallizes. If it be filtered, instead of being decanted, a brownish liquid is obtained which yields brownish crystals; but if it be boiled for some time after dilution with water, it loses its colour, deposits black flakes, and when decanted from these, yields colourless crystals. The compound is obtained less pure by boiling fulminating silver with aqueous potash, and decanting from the precipitated oxide of silver.

White, shining, somewhat elongated laminæ, which have a repulsive metallic taste, and do not blue reddened litmus-paper. Detonates very easily and with great violence. Contains 14·92 p.c. potash [=12·39 p.c. potassium]. Dissolves in 8 pts. of boiling, and in a larger quantity of cold water. Nitric acid added, not in excess, to the aqueous solution, throws down a white powder, consisting of fulminate of silver and hydrogen. Hydrochloric acid added to the solution mixed with potash, throws down a precipitate, which continues to redissolve in the liquid till

all the potassium is converted into chloride; any further quantity of the acid throws down chloride of silver, with simultaneous formation of hydrocyanic acid, carbonic acid, and sal-ammoniac. Chloride of potassium does not decompose this salt. Copper immersed in the aqueous solution, throws down all the silver, by forming fulminate of copper and potassium. The solution does not precipitate ferric sulphate, or yield prussian blue on subsequent addition of hydrochloric acid (Liebig, *Ann. Chim. Phys.* 24, 315).

Fulminate of Silver and Sodium. — Prepared by a similar process. Small, red-brown, metal-shining laminæ, containing 11·34 p.c. soda [=8·43 p.c. sodium], more soluble in water than the potash-salt, but otherwise exhibiting similar reactions (Liebig, *Ann. Chim. Phys.* 24, 316).

Fulminate of Silver and Barium. — Dingy white crystalline grains, which detonate with violence, dissolve sparingly in water, and are decomposed by hydrochloric acid, the compound dried at 100° then yielding 41·35 p.c. chloride of barium. Zinc immersed in the boiling aqueous solution throws down silver; the filtrate deposits on evaporation a yellow powder, which between 150° and 160° burns away without detonation, like cyanate of silver, leaving carbonate of baryta mixed with zinc, and when treated with hydrochloric acid, yields sal-ammoniac with effervescence, and cannot therefore be a fulminate (Liebig, *Ann. Chim. Phys.* 24, 315; *Schw.* 48, 380; Gay-Lussac & Liebig, *Ann. Chim. Phys.* 25, 302).

Fulminate of Silver and Strontium. — Dingy white crystalline grains, which detonate with violence, and are sparingly soluble in water (Liebig).

Fulminate of Silver and Calcium. — Small yellow crystalline grains, of high specific gravity, and dissolving readily even in cold water (Liebig).

Fulminate of Silver and Magnesium. — *a. Basic.* — Obtained by boiling fulminating silver with magnesia and water. Rose-coloured powder, insoluble in water, which merely decrepitates when heated, giving off carbonic acid and ammonia, and leaving a residue of magnesia and silver. — *b. Neutral.* — White, thread-like crystals, resembling capillary native silver, and detonating strongly (Liebig).

Fulminate of Silver and Zinc. — By boiling fulminating silver with zinc and water—whereby only half the silver is precipitated, even after long-continued ebullition—and evaporating the yellow filtrate, yellow detonating crystals are obtained, together with a yellow non-detonating powder (Liebig, *Ann. Chim. Phys.* 24, 308;—*Schw.* 48, 380).

Fulminate of Silver and Mercury, or *Argento-mercuric Fulminate.* — Formed by boiling fulminate of silver and hydrogen with mercuric oxide and water, or by boiling fulminating silver for not too long a time with mercury and water. From the filtrate the compound crystallizes in small shining needles (Liebig, *Ann. Chim. Phys.* 24, 305).

Zinco-auric Fulminate? — Fulminate of zinc and barium, added to a

dilute solution of normal terchloride of gold, throws down a brown, explosive compound, which dissolves even at ordinary temperatures, in ammonia, hydrochloric acid, and oil of vitriol; from the last-mentioned solution, water throws down a dark purple-red powder. — The liquid, filtered from the brown powder, yields by evaporation, yellow six-sided prisms, which explode and leave a residue of metallic gold, are insoluble in water and in hydrochloric acid, but dissolve in aqua-regia (E. Davy, *Berz. Jahresber.* 12, 128).

Zinco-platinic Fulminate? — Fulminate of zinc and barium forms with platinic sulphate a brown precipitate, which, in addition to sulphate of baryta, contains platinum and fulminic acid, and when heated, does not explode, but merely deflagrates. — The liquid, filtered from the brown precipitate, yields on evaporation the pure compound in small yellow-brown prisms, which detonate with violence (E. Davy).

Zinco-palladious Fulminate? — Fulminate of zinc forms, with nitrate of palladium, a dark-brown precipitate, which is olive-brown when dry, detonates, and is insoluble in water (E. Davy).

Conjugated Compounds of the Nitrogen-nuclei.

Trigenic Acid. $C^8N^3H^7O^4 = C^8N^2AdH^5,O^4$?

Liebig & Wöhler (1846). *Ann. Pharm.* 59, 296.

Formation. By the action of cyanic acid vapour on anhydrous aldehyde (VIII, 279).

Preparation. When cyanic acid vapour, produced by heating cyanuric acid, is passed into a few grammes of dry aldehyde contained in a vessel surrounded by cold water, the liquid becomes heated, effervesces violently from escape of carbonic acid, and fills the vessel with a froth, which ultimately solidifies in a tumid mass. With larger quantities of aldehyde, the frothing becomes too violent. — A better plan is to cool the aldehyde with ice, and leave it, after saturation with cyanic acid vapour, which then takes place quite quietly, in a moderately warm place; the effervescence then begins, and continues, like a kind of fermentation, for hours and days, till there remains either a tough half-solidified mass, or a yellowish syrup in which crystalline crusts gradually form. — The mass thus obtained, which likewise contains cyamelide, aldehyde-ammonia, and perhaps other secondary products, is dissolved in moderately strong hydrochloric acid, boiled as long as it gives off aldehyde-vapour, and filtered hot. When the filtrate is left to stand for some days in the cold, the greater part of the trigenic acid crystallizes out; the mother-liquor yields a few more crystals. The crystals are dissolved in water, decolorized by animal charcoal, and recrystallized.

Small white needles, generally in stellate groups, and having a slightly acid taste and reaction.

	Crystals.		Liebig & Wöhler.
8 C	48	37·21	38·15
3 N	42	32·56	31·24
7 H	7	5·42	5·94
4 O	32	24·81	24·67
$C^8N^3H^7O^4$	129	100·00	100·00

Decompositions. The acid when heated, melts, with decomposition and carbonization; gives off alkaline vapours smelling strongly of chinoline; and yields by dry distillation, first an alkaline, sharp-tasting distillate which smells like chinoline, and afterwards vapours off cyanic acid. The distillate solidifies in a yellowish white mass, and when distilled with potash, yields oily chinoline, while cyanuric acid remains in combination with the potash.

Combinations. The acid dissolves sparingly in *Water.*

Trigenate of Silver. The clear mixture of trigenic acid and neutral nitrate of silver, gradually mixed with dilute ammonia, deposits trigenate of silver in the form of a white powder, which appears by microscopical examination to be composed of globular crystals; assumes a violet colour when exposed to light; between 120° and 130° gives off water, and turns light brown; and at 160°, melts, blackens, and gives off a thick vapour smelling of chinoline.

	Dried at 116°.		Liebig & Wöhler.
AgO	116	49·15	48·47
8 C	48	20·34	
3 N	42	17·80	
6 H	6	2·54	
3 O	24	10·17	
$C^8N^3H^6AgO^4$	236	100·00	

Trigenic acid is nearly insoluble in alcohol (Liebig & Wöhler).

Thialdine. $C^{12}NH^{13}S^4$.

Wöhler & Liebig (1847). *Ann. Pharm.* 61, 1.

Formation and Preparation. Sulphuretted hydrogen is slowly passed for 4 or 5 hours through a solution of aldehyde-ammonia in 12 to 16 pts. of water, to which aqueous ammonia has been previously added in the proportion of 10 to 15 drops to the ounce. In half an hour, the liquid becomes white and turbid, then gradually becomes clear, and deposits large crystals resembling camphor, the appearance of which indicates the termination of the process. The crystals are drained in a funnel, washed with water, dried by pressure between paper to remove hydrosulphate of ammonia, and dissolved in ether. The solution is then mixed with one-third of its bulk of alcohol, and left to evaporate in the air; and as soon as the crystals which form are no longer covered by the mother-liquor,

this liquid is decanted and evaporated, whereby it yields a further crop of yellowish crystals, and ultimately contains nothing but hydrosulphate of ammonia:

$$3(NH^3,C^4H^4O^2) + 6HS = C^{12}NH^{13}S^4 + 2NH^4S + HO.$$

Sometimes, during the passage of the sulphuretted hydrogen, there separates, instead of the crystals, a heavy, colourless, stinking oily mixture of thialdine with a peculiar liquid. To separate the thialdine from this mixture, the greater part of the watery liquid is decanted; the oil shaken up with half its bulk of ether, which immediately dissolves it; the solution decanted from the remaining watery liquid, and well shaken up in a stoppered bottle with rather strong hydrochloric acid; the crystalline magma, consisting of needles of hydrochlorate of thialdine, washed on the filter with ether; the crystals, after drying, moistened with strong aqueous ammonia; and, lastly, heated with ether, which dissolves the liberated thialdine, and deposits it by spontaneous evaporation in the crystalline state.

Properties. Transparent, colourless, shining crystals, having the form of gypsum, and refracting light strongly. Sp. gr. 1·191 at 18°. Melts at 43°, and solidifies again in the crystalline state at 42°. Evaporates in the air at medium temperatures without residue, and may be distilled without decomposition in contact with water, but decomposes when heated alone. Has a peculiar aromatic odour, disagreeable after a while, and is neutral to vegetable colours.

	Crystals.		Wöhler & Liebig.
12 C	72	44·17	43·80
N	14	8·58	8·50
13 H	13	7·98	8·04
4 S	64	39·27	39·14
$C^{12}NH^{13}S^4$	163	100·00	99·48

$3C^4H^3S,NH^4S$ (Wöhler & Liebig.) — $C^{12}NH^{11}S^4,H^2$? Gm.

Decompositions. 1. Thialdine is resolved by dry distillation into a stinking oil, which partially solidifies after a while, and a dark brown syrupy residue containing sulphur. When distilled with hydrate of lime, at a heat rising to redness, it yields chinoline. — 3. Thialdine, or either of its salts, heated with aqueous nitrate of silver, is resolved into aldehyde which volatilizes, sulphide of silver which precipitates, and acid nitrate of ammonia which remains in solution:

$$C^{12}NH^{13}S^4 + 4(AgO,NO^5) + 2HO = 3C^4H^4O^2 + 4AgS + NH^3 + 4NO^5.$$

4. An alcoholic solution of thialdine forms a white precipitate after a few minutes, with neutral acetate of lead, then a yellow, and lastly a black precipitate; with corrosive sublimate, first white, then yellow; with bichloride of platinum, dirty yellow after a while. — 5. Thialdine forms with aqueous cyanide of mercury, a white precipitate, which by boiling is converted into sulphide of mercury; at the same time, white delicate needles sublime in the retort, very volatile, insoluble in water, but soluble in alcohol and ether; they probably consist of thialdine in which the sulphur is replaced by cyanogen.

¶ 6. Thialdine heated in a sealed tube with water and oxide of silver, is converted into leucine:

$$C^{12}NH^{13}S^4 + 4AgO = 4AgS + C^{12}NH^{13}O^4.$$

Hydrated oxide of lead effects the same transformation, but it is not so well adapted for the purpose, partly because it has a great tendency to combine with leucine, and partly because it is almost always contaminated with potash (A. Gössmann, *Ann. Pharm.* 90, 184). ¶

Combinations. Thialdine is very sparingly soluble in *Water*. — It dissolves in *Acids*, forming white crystallizable salts.

Hydrochlorate of Thialdine. — Hydrochloric acid saturated with thialdine, still retains its acid reaction. — If the thialdine was contaminated with the foreign body already mentioned, that substance exhibits its odour more strongly in the hydrochloric acid solution, but may be immediately removed by agitation with ether. — The solution, when evaporated in the air, or concentrated in the water-bath, and then cooled, yields transparent, colourless, highly lustrous prisms, often an inch long. These crystals turn brown when heated, but without melting, and yield a sublimate of sal-ammoniac, together with a gas which has a very offensive odour, and burns with a smoky flame. They dissolve in water much more readily than in alcohol, especially when heated, and are insoluble in ether.

	Crystals.		Wöhler & Liebig.
12 C	72·0	36·11	35·35
N	14·0	7·02	6·79
14 H	14·0	7·02	6·92
4 S	64·0	32·10	31·97
Cl	35·4	17·75	17·47
$C^{12}NH^{13}S^4,HCl$	199·4	100·00	98·50

Nitrate of Thialdine. — Dilute nitric acid is saturated with pure thialdine, and the solution evaporated and cooled; or the ethereal solution of impure thialdine is converted, by addition of nitric acid, into a crystalline magma, which is washed with ether, dissolved in water, and crystallized. — White delicate needles, which melt and decompose when heated. They dissolve in water more readily than the hydrochlorate, are more soluble in hot than in cold alcohol, and insoluble in ether.

	Crystals.		Wöhler & Liebig.
12 C	72	31·86	31·75
2 N	28	12·39	
14 H	14	6·19	6·36
4 S	64	28·32	28·40
6 O	48	21·24	
$C^{12}NH^{13}S^4,NO^5$	226	100·00	

Thialdine dissolves readily in *Alcohol*, and still more readily in *Ether*; its powder deliquesces when exposed to air containing ether-vapour (Wöhler & Liebig).

gründe d. theor. u. prakt. Chem. 3, 39). Thénard examined this liquid, which is in the main the same as Bunsen's alkarsin or oxide of cacodyl. But it was reserved for Bunsen's exact and laborious researches to discover not only the composition of this liquid, but also a large number of allied compounds, constituting the cacodyl-series, which he regarded as derived from a metalloïdal radical, Cacodyl = C^4AsH^6. On the other hand, Laurent (*Rev. scient.* 14, 327), Dumas (*N. Ann. Chim. Phys.* 8, 362), and Gerhardt (*Précis*, 1, 389; 2, 445) regard these compounds as belonging to the ethylene-series, and assume as the nucleus from which they are derived, the compound $C^4AsH^5 = C^4ArH^3$, analogous to ethylene, inasmuch as the cacodyl-compounds are formed from a substance belonging to the ethylene-series, viz. acetic acid; and cacodyl, when distilled with oil of vitriol, appears to yield sulphovinate of wine-oil.

Arethase. $C^4AsH^5 = C^4ArH^3$.

BUNSEN. *Ann. Pharm.* 42, 18.

Vinars (Gm.).

Preparation. By treating chloride of cacodyl, C^4AsH^6Cl, with alcoholic potash, chloride of potassium is obtained, together with a liquid which is not miscible with strong potash, and may be freed, by repeated treatment with potash and fractional distillation, from the greater part of the alcohol, which is less volatile:

$$C^4AsH^6Cl + KO = C^4AsH^5 + KCl + HO.$$

Properties. Thin, transparent, colourless liquid, almost as volatile as vinic ether, and having a repulsive ethereal odour, like that of alkarsin.

Combinations. Mixes in all proportions with *Water* and *Alcohol* (Bunsen).

Cacodyl. $C^4AsH^6 = C^4ArH^3,H$.

BUNSEN. *Ann. Pharm.* 42, 25.

Formation. May be separated from chloride of cacodyl by zinc, tin, or iron, at 90° to 100°, or from sulphide or bromide of cacodyl by mercury at 200° to 300°:

$$C^4AsH^6Cl + Zn = C^4AsH^6 + ZnCl.$$

It is also formed, together with the allied compounds, arsentrimethyl $(C^2H^3)^3As$, and arsenmethylium $(C^2H^3)^4As$, by the action of iodide of methyl on arsenide of sodium (Cahours & Riche, *Compt. rend.* 39, 542; see also page 351 of this volume).

Preparation. Pure zinc and pure chloride of cacodyl are heated together to 100° for three hours, in a perfectly closed vessel; the resulting

chloride of zinc removed by water; and the cacodyl, which sinks to the bottom in the form of an oil, dehydrated by chloride of calcium.

The details of this operation, which is rendered very difficult by the strong tendency of cacodyl to take fire in the air, are as follows: To obtain chloride of cacodyl perfectly free from alkarsin (p. 320), the alkarsin is digested three times with strong hydrochloric acid, till the resulting chloride of cacodyl no longer emits the slightest fume on exposure to the air. It is then digested for several days with a mixture of chloride of calcium and lime, to free it completely from water and hydrochloric acid. For this purpose, a glass tube having a bulb in the middle and placed in a vertical position, is bent upwards at an acute angle at the lower part, and again vertically downwards at the same acute angle; the bulb contains a mixture of lime and chloride of calcium. Through the upper end of this apparatus (1), dry carbonic acid gas is passed to expel the air; the lower end dipped into the chloride of cacodyl below the hydrochloric acid; the chloride of cacodyl drawn up into the apparatus by means of a hand-pump attached by a caoutchouc tube to the upper end; and lastly, the two ends sealed, and the apparatus set aside for some days. — To decompose the cacodyl thus purified, with zinc, the following apparatus (2) is used: A glass tube passes for a short distance obliquely upwards; is then bent at an acute angle vertically downwards; then at the same acute angle obliquely upwards; and in the middle of this arm, is blown into a bulb; it then passes at the same acute angle, but for a greater length, vertically downwards, and is in this part again blown into a bulb; lastly, it is bent at short distances and at acute angles, first obliquely upwards, then vertically downwards. The upper bulb of this apparatus is filled with thin zinc-foil, which has been treated with dilute sulphuric acid, then washed with water, dried, and cut up into spiral slips; the apparatus carefully filled with dry carbonic acid gas; the chloride of cacodyl sucked into the upper bulb; both ends of the tube sealed; and the apparatus heated for three hours in the water-bath. The zinc dissolves without evolution of gas, the liquid becoming somewhat darker. The liquid, as it cools to + 50°, deposits large cubical crystals, probably a compound of chloride of zinc with chloride of cacodyl, which disappear again on heating the liquid. Ultimately, when the chlorine is completely removed, the contents of the bulb appear at 100° as a dry white mass, which melts again to an oil between 110° and 126°. The lower end of the still hot apparatus is now dipped into water which has been thoroughly boiled and cooled; then broken off, so that the water may enter as the apparatus cools; then sealed, and the whole inclined so that the water may run from the lower bulb into the upper, where, after digestion for some time, it dissolves the chloride of zinc, leaving the cacodyl in the form of an oil, together with the excess of zinc. The cacodyl is then dried in apparatus (1), again drawn into apparatus (2), and again digested with pure zinc, by which operation however only a small quantity of chloride of zinc is now formed. The cacodyl is then distilled from the upper bulb into the lower; the transparent, colourless distillate cooled to —6°, till two-thirds have crystallized out; and the portion which still remains fluid poured back into the upper bulb, again digested with zinc, again distilled, and so on three times more. By this series of operations, pure cacodyl is at length obtained in the lower bulb.

Properties. Crystallizes at —6° in large shining square prisms. At ordinary temperatures, it forms a thin, transparent, colourless, strongly

refracting oil, heavier than water. Boils near 170°. Vapour-density = 7·101. Has the odour of alkarsin.

		Bunsen.		Vol.	Density.
4 C	24	22·86	22·27	C-vapour 4	1·6640
As	75	71·43	71·15	As-vapour ½	5·1998
6 H	6	5·71	5·40	H-gas 6	0·4158
C^4ArH^3,H	105	100·00	98·82	Cacodyl-vapour 1	7·2796

Bunsen, adopting the radical-theory, regards cacodyl as a metalloïdal radical, corresponding to ethyl, C^4H^5, and other radicals assumed by this theory but hitherto unisolated [this was written before the isolation of ethyl, methyl, &c]; and the isolation of cacodyl, in addition to that of cyanogen, and perhaps of mellone, is looked upon as a great support of the radical-theory. It is however remarkable that cacodyl boils at 170°, whereas alkarsin, its compound with 1 At. oxygen, boils at 150°, though in other cases the boiling point of organic compounds is raised by addition of oxygen. Cacodyl might therefore be regarded as a conjugated compound = $C^8As^2H^{12} = C^4ArH^3,C^4ArH^3,H^2$. — Bunsen denotes cacodyl by the symbol Kd. Berzelius (*Jahresber.* 24, 641) uses the symbol Kk. The latter regards cacodyl as a compound of acetyl with arseniuretted hydrogen = C^4H^3,AsH^3, and consequently all compounds of the cacodyl-series as compounds of arseniuretted hydrogen with acetyl and its compounds. — ¶ Cacodyl may also be regarded as a compound of 1 At. arsenic with 2 At. methyl = $(C^2H^3)^2As$; accordingly Frankland (*Chem. Soc. Qu. J.* VI, 71) calls it *Bimethide of arsenic*. This view of its constitution is supported by the fact of its formation, together with the compounds $(C^2H^3)^3As$ and $(C^2H^3)^4As$, by the action of iodide of methyl on arsenide of sodium (p. 351), just as arsenbiethyl and the other arsenethyls are obtained by the action of iodide of ethyl on arsenide of sodium.* ¶

Decompositions. 1. Cacodyl heated in a bent tube closed at top, to a temperature somewhat above the boiling point of mercury, is resolved, without deposition of carbon, into arsenic and a mixture of 2 vol. marsh-gas and 1 vol. olefiant gas:

$$2C^4AsH^6 = 2C^2H^4 + C^4N^4 + 2As.$$

The gaseous mixture contains also a small quantity of cacodyl vapour, whence it burns with a coloured luminous flame, depositing a small quantity of arsenic, and when mixed with chlorine over water, takes fire and burns with a fiery red light, and deposition of charcoal. Oil of vitriol abstracts the olefiant gas and cacodyl vapour from the mixture, leaving the marsh-gas. 6 vol. of the gaseous mixture exploded with oxygen consume 14 vol. oxygen and produce 8 vol. carbonic acid gas. [4 vol. marsh-gas consume 8 vol. oxygen and produce 4 vol. carbonic acid gas; 2 vol. olefiant gas consume 6 vol. oxygen and produce 4 vol. carbonic acid = 4 + 2 : 8 + 6 : 4 + 4.] — 2. When cacodyl is distilled with dry chloride of zinc, liquids of various boiling point pass over, apparently consisting of mixtures of a hydrocarbon, undecomposed cacodyl, and a peculiar arsenic-compound. — When zinc is digested with chloride of cacodyl in apparatus (2), p. 317, till it is completely converted into a white crystalline mass, and this mass quickly heated in the oil-bath, a colourless liquid passes over from 200° to 260°, without any evolution of gas. If this liquid be drawn up into another apparatus (2); there freed

* According to Gmelin's arrangement, arsenbiethyl should be placed in the 8-carbon series, and regarded as C^8ArH^7,H; and similarly Landolt's arsentriethyl, $C^{12}H^{15}As$, might be regarded as $C^{12}(AsH^3)H^{11},H$; and arsenethylium, $C^{16}H^{20}As$, as $C^{16}(AsH^4)H^{15},H$, the former of these two compounds containing AsH^3, analogous to ammonia, and the latter containing AsH^4, analogous to ammonium. As however there can be but little doubt that these compounds really belong to the ethyl-series, being in fact produced from iodide of ethyl, it has been thought best to place them in that series. [W.]

from the remaining chlorine by longer digestion with zinc; then distilled in the oil-bath, first at 90° to 100°, then at 100° to 170°, and lastly at 170° to 200°; and each of these three distillates collected apart, by drawing up the residue left after the first distillate into a fresh apparatus, there continuing the distillation to 170°, and heating the residue to 200° in a fresh apparatus (2): all the three distillates thus obtained are transparent, colourless and mobile. The first remains liquid at −18°; has a peculiar odour; contains but a small quantity of cacodyl; and scarcely takes fire in the air. The second and third distillate yield at −8°, large prisms of cacodyl, and take fire very readily on exposure to the air. These distillates have the following constitution:

	From 90° to 100°.	From 100° to 170°.	From 170° to 200°.
C	28·95	26·31	19·88
As	64·31	67·15	75·53
H	7·26	6·46	4·82
	100·52	99·92	100·23

3. Cacodyl takes fire in the air at ordinary temperatures even more readily than alkarsin. Its combustion yields carbonic acid, arsenious acid, and water; if the quantity of air present be not sufficient for complete combustion, erythrarsin is immediately deposited, together with a black crust of arsenic having a very offensive odour. When an attempt is made to pour out a drop of this liquid, it takes fire even before it separates from the lip of the bottle; a thread of glass moistened with cacodyl takes fire immediately on exposure to the air.—With scanty access of air, cacodyl emits white fumes, and is converted, according to the quantity of oxygen present, partly into alkarsin, partly into cacodylic acid. From the alkarsin thus obtained, chloride of cacodyl, &c. may be reproduced by the action of hydrogen-acids, and from this again the cacodyl itself.

4. In chlorine gas, cacodyl takes fire at ordinary temperatures, burning with a red flame and depositing charcoal. By chlorine-water, it is instantly converted into chloride of cacodyl.

5. By dissolving a comparatively small quantity of sulphur, it is converted into protosulphide of cacodyl, C^4AsH^6S; and by taking up a larger quantity, into the persulphide, $C^4AsH^6S^3$, which separates from ether in large crystals.

6. By solution in nitric acid, it is converted into alkarsin, and with the aid of heat, into cacodylic acid.

7. It dissolves in fuming sulphuric acid without blackening, but even at ordinary temperatures eliminates a large quantity of sulphurous acid gas, and afterwards yields by distillation, a substance having a pleasant ethereal odour, and apparently consisting of sulphovinate of wine-oil.

8. By digestion with hydrochloric acid and zinc, it yields a number of products, among which is erythrarsin. It likewise appears to yield this body when treated with phosphorous acid, protochloride of tin, and other powerful reducing agents (Bunsen).

¶ Cacodyl mixed with iodide of methyl yields *iodide of arsenmethylium*, Me^4As,I, and iodide of cacodyl:

$$2C^4H^6As + 2C^2H^3I = (C^2H^3)^4AsI + C^4H^6I.$$

Similarly with iodide of ethyl, it yields *iodide of arsenmethylethylium* $(C^2H^3)^2(C^4H^5)^2AsI$, and iodide of cacodyl; and with iodide of amyl,

iodide of arsenmethylammonium $(C^2H^3)^4(C^2H^3)^4AsI$, and iodide of cacodyl. In those two latter cases, however, the action does not take place without the aid of heat (Cahours & Riche, *Compt. rend.* 38, 543; see also pages 351, 225 of this volume). ¶

Oxide of Cacodyl or Alkarsin. $C^4AsH^6O = C^4AsH^3,HO$.

Cadet. *Mem. de Math. et Phys. present. des Savans étrang.* 3, 633; also *Crell. Neust. chem. Arch.* 1, 212.
Thenard. *Ann. Chim.* 52, 54; also *Bull. philom. Nr.* 86, 202; also *A. Gehl.* 4, 292.
Bunsen. *Pogg.* 40, 219; — 42, 145. — *Ann. Pharm.* 37, 6; 42, 19.
Dumas. *Ann. Pharm.* 27, 148. — *N. Ann. Chim. Phys.* 8, 362.

Acetite oleoarsenical (Thénard). [*Leuminaire*].—For the history, see pp. 315, 316.

Formation. By heating acetate of potash and various other acetates with an equal weight of arsenious acid. — [If the numerous other products, formed at the same time, may be regarded, not as essential, but as perhaps produced by an excess of arsenious acid and too much heat, the equation will be:

$$2C^4H^3KO^4 + AsO^3 = C^4AsH^6O + 2(KO,CO^2) + 2CO^2].$$

Berzelius supposes, almost in the same way, that the alkarsin is produced from anhydrous acetic acid, according to the following equation:

$$2C^4H^3O^3 + AsO^3 = C^4AsH^6O + 4CO^2;$$

and Bunsen supposes it to be produced from the acetone evolved by the acetate of potash, according to this equation:

$$C^3H^6O^2 + AsO^3 = C^4AsH^6O + 2CO^2.$$

When acetate of potash is distilled with an equal weight of arsenious acid, large quantities of carbonic acid, carburetted hydrogen, and arseniuretted hydrogen gases are evolved; metallic arsenic sublimes; and in the receiver surrounded with ice and salt, two distillates condense. The lower pale yellow liquid, in which a few particles of arsenic float, is Cadet's liquid [impure alkarsin]; the upper, which is brownish-yellow, watery acid, and less fuming, may be regarded as a solution of the lower liquid in aqueous acetic acid (Thénard).

In this distillation, large quantities of carbonic acid and marsh-gas are given off, together with a little olefiant gas and much alkarsin vapour, but no arseniuretted hydrogen; and the products collected in the receiver consist of metallic arsenic at the bottom, — above this, a brown oily mixture of alkarsin with small quantities of erythrarsin, acetic acid and arsenious acid, amounting to 30 per cent of the arsenious acid used, — and at top, a solution of alkarsin and arsenious acid in acetone, acetic acid, and water. Carbonate of potash remains in the retort (Bunsen).

Preparation. Acetate of potash is mixed with an equal weight of arsenious acid in a glass retort fitted with a well cooled receiver and placed in the open air; the mixture gradually heated to redness, till it ultimately melts from formation of carbonate of potash; and the receiver

removed after the liquid has completely cooled, but not before, lest the liquid in the neck of the retort should take fire. The upper watery distillate is then poured off; the brown oily distillate quickly transferred to a flask and repeatedly shaken up with water; and the remaining acetic acid, arsenious acid, and erythrarsin removed, either by rectifying the oily liquid over hydrate of potash in an apparatus filled with carbonic acid, or better by distilling it under a stratum of deaerated water. The colourless rectificate is separated from the greater part of the water by mechanical means, and from the remainder by distillation over baryta or lime out of contact of air (Bunsen). — This operation may be performed in a glass tube bent knee-shape at an obtuse angle, having the right arm longer than the left, and at the extremities, bulbs terminating in fine necks. After the left-hand bulb has been filled with small fragments of baryta, this apparatus (3) is filled with carbonic acid or hydrogen gas; the neck of the empty right-hand bulb sealed; this bulb heated; and the neck of the left-hand bulb dipped into the liquid, which then rises into the left-hand bulb as the right-hand bulb cools. The neck of the left-hand bulb is then likewise sealed; and the distillation effected by carefully heating the left hand bulb with a spirit-lamp, while the right arm of the tube and its bulb are kept cool with cold water. (If the heat be too powerful or too long continued, permanent gases are evolved which burst the apparatus, producing a flame several feet high, which covers the surrounding objects with a black film of stinking arsenic). Finally, the distillate is twice poured back from the right to the left hand bulb, and twice redistilled. — The transference of the pure alkarsin thus obtained in the right hand bulb, into other smaller bulbs, is performed in an atmosphere of carbonic acid, so as completely to exclude the air. The neck of the left-hand bulb is first opened, so that the air which enters may be completely deprived of oxygen by the remaining liquid; the right arm of the tube then scratched and broken off; and through this, the long necks of the bulbs which are to be filled, are inserted into the distillate in the bulb, after they have been filled with carbonic acid or hydrogen and heated, so that the liquid may be drawn up into them as they cool; the necks are then sealed For further details see *Pogg.* 42, 147. Alkarsin may also be very well preserved under water in a stoppered bottle (Bunsen.)

Thénard purified Cadet's liquid by one rectification only.

Properties. Alkarsin solidifies at −25° in crystalline scales having a silky lustre. At ordinary temperatures, it is a transparent colourless liquid of strong refracting power. Sp gr. 1·462 at 15°. Boiling point about 150°. Vapour-density 7·555. Fumes strongly in the air. Has an intensely offensive odour which adheres to the clothes for months; excites a copious flow of tears, and an intolerable persistent irritation in the mucous membrane of the nose. The vapour inhaled together with air, produces nausea and oppression of the chest, and in delicate persons immediate vomiting; it appears chiefly to affect the nerves, but without causing any permanent injury to the health. Alkarsin placed upon the skin, if it does not take fire, produces slight inflammation, attended with violent itching, which may be alleviated by plasters of ferric acetate; but in most cases, it takes fire almost instantly and produces dangerous burns. It is neutral to vegetable colours (Bunsen). — Oily; perfectly volatile; and when exposed to the air, emits dense white fumes having a terribly offensive arsenical odour and stupifying action (Thénard).

			Bunsen.		Dumas.		Vol.	Density.
4 C	24	....	21·24	....	21·71	.... 22·48	C-vapour 4	.... 1·6640
As	75	....	66·37	....	65·75	.... 69·08	As-vapour ..... ½	.... 5·1998
6 H	6	....	5·31	....	5·30	.... 5·66	H-gas 6	.... 0·4158
O	8	....	7·08	....	7·24		O-gas ..... ½	.... 0·5546
C^8ArH^3,HO	113	....	100·00	....	100·00	.... 97·22	Alkarsin-vapour 1	.... 7·8342

Vinic ether, in which 1H of the nucleus is replaced by AsH^2 or Ar. — Dumas, from his own analysis, regards alkarsin as C^4AsH^6 [which would be cacodyl]. Bunsen also at first overlooked the O, till Berzelius drew attention to the probability of its presence.

Decompositions. When alkarsin vapour is heated, not quite to redness, permanent gases are formed, and arsenic and erythrarsin precipitated.

2. Alkarsin exposed to the air gives off white fumes, becomes heated by rapid absorption of oxygen, and quickly bursts into a greyish flame, forming arsenious acid, carbonic acid, and water. A drop of it falling through the air takes fire before it reaches the ground. According to Thénard, it takes fire in the air only when it contains particles of arsenic. — If the spontaneous inflammation of alkarsin be prevented by keeping it very cold, or by slowly admitting air to it through a small aperture, it is gradually converted, with rise of temperature, into a viscid syrup mixed with crystals of cacodylic acid; the syrup has the composition $C^4AsH^6O^2 = C^4AsH^6O,C^4AsH^6O^3$, and may therefore be regarded as anhydrous cacodylate of cacodyl; it dissolves without decomposition in a small quantity of water, but on the addition of a larger quantity, deposits paracacodylic oxide in the form of an oil, while cacodylic acid, together with a large quantity of paracacodylic oxide remains in solution; on distilling the syrup, the greater portion of the paracacodylic oxide distils over between 120° to 130°. The syrup scarcely undergoes any further oxidation when exposed to the air at ordinary temperatures; but when air or oxygen gas is passed through it for several days at a temperature of 60° to 70°, the greater portion is converted into crystallized cacodylic acid. — [According to Bunsen, paracacodylic oxide is isomeric with cacodylic oxide; the cacodylic acid is perhaps formed in the manner represented by the equation:

$$C^4AsH^6O + 2O + HO = C^4AsH^7O^4.$$

According to this equation, alkarsin could not form cacodylic acid by oxidation in perfectly dry air, unless a product containing less than 6H were formed at the same time. The action of dry air upon alkarsin requires therefore to be further examined.] — If the access of air be too rapid, arsenious acid is likewise formed. — Alkarsin kept under water in an open vessel, slowly disappears, forming compounds soluble in water [cacodylic acid?] (The formation of crystals was observed by Thénard).

3. Alkarsin instantly takes fire in chlorine gas, burning with a yellow, smoky flame, and forming chloride of arsenic and hydrochloric acid. But the resulting liquid, when diluted with water and treated with sulphuretted hydrogen, does not yield all the arsenic in the form of sulphide,—a proof that part of the arsenic is contained in it, not as chloride of arsenic, but still in the form of an organic compound. — After the combustion, arsenic, arsenious, and acetic acid are found to have been produced (Thénard). — 4. Bromine in contact with alkarsin produces heat nearly sufficient to set the compound on fire, and precipitates brown flocks. — 5. Iodine dissolves

in alkarsin, forming a colourless liquid, which deposits a white crystalline body, soluble in a larger quantity of iodine.

6. Alkarsin explodes with fuming nitric acid, producing a large bright flame. By cold concentrated or hot dilute nitric acid, it is converted into cacodylic acid: the cacodylic acid is not completely decomposed, even by continued heating with nitric acid in a sealed glass tube. —Alkarsin likewise explodes with aqua-regia (Dumas).

7. Alkarsin reduces in the moist way the oxides of mercury, silver and gold, arsenic acid, and indigo [with formation of cacodylic acid?]. — Ignited in a combustion-tube with oxide of copper, it yields carbonic acid, water, arsenide of copper in small shining crystals, and small quantities of arsenious acid and cupric arseniate.

8. With hydrogen-acids, alkarsin yields water, and a compound ether in which the oxygen of the alkarsin is replaced by the radical of the acid.

9. Potassium heated with alkarsin produces a fiery explosion, whereby charcoal appears to be separated and arsenide of potassium formed; at ordinary temperatures, the potassium remains bright for a while, but is then slowly converted, with slight evolution of gas, into a white magma.

10. With aqueous cyanide of mercury, alkarsin forms cyanide of cacodyl, the mercury being reduced, and the alkarsin partially brought to a state of higher oxidation (Bunsen).

Combinations. Alkarsin dissolves very sparingly in *Water,* imparting to the liquid its peculiar penetrating odour.

It dissolves *Phosphorus,* producing an opalescent liquid.

It dissolves abundantly in aqueous *Phosphoric acid,* forming a stinking, acid, uncrystallizable liquid, which when heated, is resolved into water, alkarsin, and a residue of phosphoric acid.

With the aid of heat, it dissolves *Sulphur* in all proportions, forming a red liquid, from which the sulphur separates in radiating crystals on cooling.

When digested with non-fuming *oil of vitriol,* it forms a liquid which solidifies on cooling in a mass of needle-shaped crystals; these crystals, when purified by pressure between paper, have an extremely offensive odour, an acid reaction, and deliquesce in the air.

It dissolves without decomposition in cold, moderately dilute *Nitric acid,* forming a thick liquid, which, with many heavy metallic salts, yields peculiar and very unstable precipitates.

It dissolves in aqueous *Potash,* forming a brown liquid:

Alkarsin with Mercuric Bromide. Probably $= 2HgBr,C^4ArH^4O$. — Separates in the crystalline form on mixing [alcoholic?] mercuric bromide with alkarsin dissolved in a large quantity of alcohol (even with alkarsin which has been slowly oxidized by exposure to the air), and may be purified by recrystallization. — Pale yellowish-white crystalline powder or laminæ; inodorous, but has a disgusting metallic taste. — Fuses without decomposition when gently heated in a close vessel, and at a higher temperature, yields a sublimate of mercurous and mercuric bromide, a stinking distillate containing bromine, and a residue of charcoal. When heated in the air, it volatilizes without residue, and with partial combustion. Decomposes when its aqueous solution is boiled. Exhibits moreover the same reactions and the same degree of solubility in water as the following chlorine compound.

Alkarsin with Mercuric Chloride. $2HgCl,C^4ArH^4O$. — A dilute alcoholic solution of alkarsin (even that which has been slowly oxidized in the air) mixed with dilute [alcoholic?] solution of corrosive sublimate, in quantity not quite sufficient to remove the odour of alkarsin, yields this compound in the form of a white bulky precipitate mixed with calomel. By pressing the precipitate between paper, boiling up in water, filtering, and three times crystallizing, the compound is obtained pure. If the mercurial solution be added in excess, so as completely to destroy the odour of alkarsin, the compound is decomposed by this excess and calomel is then often the only product. — Instead of alkarsin, cyanide of cacodyl or other compounds of 1 At. cacodyl with 1 At. of a salt-radical may be used.

The compound separates from the aqueous solution, when quickly cooled, in soft, nacreous scales, and by very slow cooling, in small rhombic tables with angles of about 60° and 120°. Although otherwise perfectly inodorous, it causes, when a particle is inhaled into the nose, a most intolerable and persistent odour. When placed on the tongue, it excites a disagreeable metallic taste, and produces nausea even in the smallest quantity; in larger quantity, it is extremely poisonous.

					Bunsen.
4 C	24·0	....	6·25	.....	6·23
As	75·0	....	19·54	.....	19·25
6 H	6·0	....	1·57	.....	1·76
O	8·0	....	2·08	.....	3·94
2 Hg	200·0	....	52·11	.....	50·80
2 Cl	70·8	....	18·45	.....	18·02
$2HgCl + C^4ArH^3,HO$	383·8	....	100·00	.....	100·00

In consequence of the difficulty of the analysis, Bunsen obtained too much oxygen: more recently (*Ann. Pharm.* 46, 40) he gives the preference to the less probable formula, $KkCl^2,Hg^2O$.

The compound is readily decomposed by heat, and when subjected to dry distillation, yields a sublimate of mercurous and mercuric chloride and erythrarsin, besides stinking vapours, and leaves a porous charcoal which burns away in the air without residue, diffusing an arsenical odour. The compound likewise suffers decomposition and volatilizes completely, when heated in the air. — When the aqueous solution is boiled alone, the compound is resolved (more quickly in presence of excess of corrosive sublimate) into chloride of cacodyl which volatilizes, calomel which is precipitated, and corrosive sublimate and cacodylic acid which remain in solution. [Probably thus:

$$2(C^4AsH^6O,2HgCl) + 2HO = C^4AsH^6Cl + C^4AsH^7O^4 + 2Hg^2Cl + HCl.$$

According to this equation, there should be formed, not protochloride of mercury, but hydrochloric acid; the latter might, however, at a boiling heat decompose part of the calomel into corrosive sublimate and metallic mercury. It is a question, therefore, whether the calomel which remains is mixed with mercury. At all events, Bunsen's equation (*Ann. Pharm.* 37, 46):

$$4(C^4AsH^6O,2HgCl) = 3C^4AsH^6Cl + 3Hg^2Cl + 2HgCl,$$

s inadmissible, inasmuch as it supposes cacodylic acid to contain only 6H]. — Aqueous hydriodic acid, in contact with alkarsin, immediately

forms red iodide of mercury, which dissolves in the excess of acid, with separation of yellow oily drops of iodide of cacodyl:

$$[C^4AsH^6O,2HgCl + 3HI = C^4AsH^6I + 2HgI + 2HCl + HO.$$

Bunsen gives a somewhat different equation, according to which a compound of 2 At. corrosive sublimate with 1 At. hydriodic acid would be formed]. — Hydrochloric acid decomposes the compound in a similar manner into chloride of cacodyl, corrosive sublimate, and water:

$$C^4AsH^6O,2HgCl + HCl = C^4AsH^6Cl + 2HgCl + HO.$$

Other hydrogen-acids behave in a similar manner. — Aqueous phosphoric acid exerts scarcely any decomposing action upon alkarsin, and forms therewith an aqueous distillate which smells of chloride of cacodyl, but contains only traces of it. — Easily reducible metallic oxides, and likewise terchloride of gold, are reduced by this compound, with formation of cacodylic acid, just as by free alkarsin. — On the other hand, by distillation with phosphorous acid, calomel is separated and protochloride of cacodyl obtained; and similarly with tin, mercury, and other substances which reduce corrosive sublimate:

$$2(C^4AsH^6O,2HgCl) + PO^3 = 2C^4AsH^6Cl + 2Hg^2Cl + PO^5.$$

When a solution of the compound is decomposed by less than an equivalent quantity of potash, yellow mercuric oxide is precipitated, and converted by the liberated alkarsin and undecomposed corrosive sublimate, into calomel. On further addition of potash, the calomel is converted into mercurous oxide, which then raises the alkarsin to a higher state of oxidation, and is itself thereby reduced. — The compound dissolves in 477 pts. water at 18°, and in 288 pts. of boiling water; it likewise dissolves in cold, and more readily in hot alcohol.

Alkarsin with Nitrate of Silver. $3C^4ArH^4O + AgO,NO^5$. — When alkarsin is dissolved in moderately strong nitric acid, care being taken to avoid all rise of temperature, and the solution diluted with water and mixed with nitrate of silver, a copious white, granular, quickly sinking precipitate is formed, which must be washed by decantation with water free from air. — This precipitate in the pure state forms a white crystalline powder, and when examined with a lens, appears to be composed of regular octohedrons with truncated edges and summits, and of octohedral segments; the crystals have an adamantine lustre. It decomposes on exposure to light or air, or in contact with organic bodies, assuming first a yellowish, then a brownish colour. After drying over oil of vitriol, it does not give off water or undergo any other alteration at 90°. At 100°, it explodes with fire, emitting products of decomposition having an offensive odour. It does not dissolve in cold nitric acid, but is rapidly oxidated by that acid at higher temperatures. When boiled with aqueous nitrate of silver, it reduces the metal in the specular form. It is decomposed but slowly by aqueous chloride of barium, chloride of silver and nitrate of baryta being formed, besides volatile cacodyl-compounds.

	Crystallized.			Bunsen.
12 C	72	....	14·15	..... 14·50
3 As	225	....	44·20	..... 45·54
18 H	18	....	3·53	..... 3·57
Ag	108	....	21·22	..... 21·49
N	14	....	2·75	..... 2·89
9 O	72	....	14·15	..... 12·01
$3C^4AsH^6O + AgO,NO^5$	509	....	100·00	..... 100·00

Alkarsin mixes in all proportions with *Alcohol* and *Ether*, and is separated from the solutions by water in its original state.

It forms compounds with *Iodide*, *Bromide*, and *Chloride of Cacodyl*.

Paracacodylic Oxide. $C^4AsH^6O=C^4ArH^3,HO$.

Bunsen. *Pogg.* 42, 15.

When air is admitted to alkarsin so slowly that no heating or inflammation takes place, the alkarsin is converted into a syrup filled with crystals of cacodylic acid; the absorption of oxygen becoming continually slower. The resulting tenacious mass, when dissolved in water and distilled, yields, first a watery liquid smelling of alkarsin, then between 120° and 130°, an oil sparingly soluble in water, which is dried over baryta and purified by distillation out of contact of air. — After the first distillation, during which the temperature should not rise so high as 135°, a residue is left consisting of cacodylic acid and a trifling quantity of arsenious acid, still mixed with paracacodylic oxide. The cacodylic acid produced by the slow oxidation of the alkarsin, probably unites with the rest of the alkarsin, forming a saline compound which offers greater resistance to oxidation; and during the distillation, the alkarsin separates again, in the form of its isomeric compound, paracacodylic oxide, from the cacodylic acid; it must, however, be observed that alkarsin may likewise be distilled from its compound with phosphoric acid, at about 130°, without being thereby converted into paracacodylic oxide.

Transparent, colourless oil, which has a peculiar penetrating odour, boils at 120°, and does not fume in the air (Bunsen).

			Bunsen.
4 C	24	21·24	21·64
As	75	66·37	63·03
6 H	6	5·31	5·12
O	8	7·08	10·21
C^4AsH^6O	113	100·00	100·00

The determination of the arsenic was attended with a slight loss.

Paracacodylic oxide when exposed to the air, is converted very slowly, and without perceptible rise of temperature, into cacodylic acid. Air saturated with its vapour at 50° to 70°, explodes with great violence when set on fire. — With hydrogen-acids it behaves like alkarsin. — But with aqueous cyanide of mercury, it does not, like alkarsin, form cyanide of cacodyl, but yields a brown, pulverulent precipitate, resembling paracyanogen, and smelling like dried morels.

It dissolves sparingly in water, and behaves with other solvents, as well as towards protochloride of mercury, nitrate of silver, and bichloride of platinum, like alkarsin.

Cacodylic Acid or Alkargen. $C^4AsH^7O^4$.

BUNSEN. *Pogg.* 22, 145. — *Ann. Pharm.* 46, 2.

Formed by the slow oxidation of alkarsin in the air or in oxygen gas (pp. 318 and 322), by the oxidation of the same compound by concentrated or heated nitric acid, by mercuric oxide, silver-oxide or auric oxide (*Ann. Pharm.* 37, 14); and together with persulphide of cacodyl, when the protosulphide oxidizes in the air.

Preparation. Air is brought in contact with alkarsin, so slowly, that no inflammation takes place; oxygen gas or air passed for several days through the resulting syrup contained in a tubulated retort at a temperature of 60° to 70°, till nearly the whole is converted into crystallized cacodylic acid; the greater part of the excess of paracacodylic oxide removed by distilling it between 130° and 140°; and the cacodylic acid freed from the rest of the paracacodylic oxide by pressure between paper, and two crystallizations from absolute alcohol. This process yields cacodylic acid pure, but in small quantity only, because the greater portion is volatilized during the passage of the oxygen gas through the heated syrup; at the same time the air is disagreeably infected by it.

2. Better: Alkarsin is brought in contact with mercuric oxide under water; the mixture prevented from rising to a boiling heat, by cooling from without, or by pouring cold water into it; the liquid, as soon as it ceases to smell of alkarsin and has become clear, decanted from the reduced mercury, and—in order to decompose the mercuric oxide which has been formed—mixed drop by drop with alkarsin, till no more mercury separates out on heating the mixture, and a faint odour of alkarsin becomes perceptible; then evaporated; the residue dissolved in alcohol; and the cacodylic acid allowed to crystallize out, and purified by recrystallization from alcohol. By this process, 76 pts. of alkarsin treated with 218 pts. of mercuric oxide, yield 88 pts. of cacodylic acid. [According to Bunsen's formula of cacodylic acid, $C^4AsH^7O^4$, the equation is:

$$C^4AsH^6O + 2HgO + HO = C^4AsH^7O^4 + 2Hg.$$

According to this equation, 113 pts. (1 At.) alkarsin treated with 216 pts. (2 At.) mercuric oxide should yield 138 pts. (1 At.) cacodylic acid, = 76 (alkarsin): 145 (mercuric oxide): 92·8 (cacodylic acid). — According to the formula of cacodylic acid proposed by Gerhardt (*Précis*, 2, 445), and previously also by Laurent, viz., $C^4AsH^5O^4$, the equation is:

$$C^4AsH^6O + 4HgO = C^4AsH^5O^4 + 4Hg + HO.$$

According to this equation, 113 pts. of alkarsin and 432 pts. of mercuric oxide, yield 136 pts. of cacodylic oxide = 76 : 290·5 : 91·5. — Now, according to Bunsen, 218 pts. of mercuric oxide are sufficient to convert 76 pts. of alkarsin into cacodylic acid, whereas Gerhardt's calculation requires 290·5 pts. of mercuric oxide to produce the same effect; the result is therefore very unfavourable to Gerhardt's formula of cacodylic acid].

Properties. The acid crystallizes from alcohol in large, transparent, colourless, oblique rhombic prisms. The form is nearly that of *Fig.* 106; $i : t = 97° 27'$; $u : u$ backwards $= 119° 52'$. The crystals when heated to 200°, do not give off water, but emit a pungent arsenical odour, assume a brownish colour, and melt into an oil, which solidifies at 90°, forming a radiated mass. The acid is inodorous, has a slightly sour taste and acid reaction, and does not exhibit any poisonous action. — 6 grains of the acid injected into the stomach of a rabbit, or 7 grains into the jugular vein, or 4 grains into the lungs, do not appear to produce the slightest uneasiness.

Calculation according to Bunsen			Calculation according to Gerhardt.			Bunsen.
4 C	24	17·39	4 C	24	17·65	17·44
As	75	54·35	As	75	55·15	56·27
7 H	7	5·07	5 H	5	3·67	5·01
4 O	32	23·19	4 O	32	23·53	21·28
$C^4AsH^7O^4$	138	100·00	$C^4AsH^5O^4$	136	100·00	100·00

The quantity of arsenic found by Bunsen, agrees best with Gerhardt's formula, the amount of hydrogen with Bunsen's. — Bunsen assumes also the existence of a hypothetical anhydrous cacodylic acid, $= C^4AsH^6O^3$, which, with HO, is supposed to form the crystallized acid. According to Gerhardt's formula, crystallized cacodylic acid is glacial acetic acid, in the nucleus of which 1 At. hydrogen is replaced by 1 At. arsidogen $=$ Ar $= AsH^2$. Simple as this hypothesis may appear, it accords but little with Bunsen's exact analyses of cacodylic acid, which give more hydrogen than Gerhardt's formula admits (see the following tables). On this hypothesis also, many of the equations become more complicated than when Bunsen's is adopted; moreover, the above explained formation of cacodylic acid from alkarsin and mercuric oxide is altogether subversive of it, unless Bunsen's statements are affected by serious numerical errors. Nevertheless, Bunsen's formula, $C^4AsH^7O^4$, is as unfavourable to the radical as to the nucleus theory. The radical theory regards cacodyl, C^4AsH^6, as analogous to ethyl, C^4H^5. Now $C^4H^5 + O$ is oxide of ethyl, and $C^4AsH^6 + O$ is oxide of cacodyl; so far the analogy holds good; but $C^4H^5 + O^3$ is $C^4H^3O^3$ (hypothetical anhydrous acetic or ethylic acid) $+ 2HO$; whereas $C^4AsH^6 + O^5 = C^4AsH^4O^3 + 2HO$; and yet, hypothetical anhydrous cacodylic acid is not $C^4AsH^4O^3$, but $C^4AsH^6O^3$.

Laurent (*N. Ann. Chim. Phys.* 22, 109) has recently admitted Bunsen's formula of cacodylic acid, and compares that acid with acetate of ammonia, $NH^3,C^4H^4O^4$, supposing the ammonia NH^3 to be replaced by arseniuretted hydrogen, AsH^3. According to this hypothesis, cacodylic acid is an acetate of arseniuretted hydrogen. If the formula of acetic acid be written in such a form, that the 1 At. H which is replaceable by metals, may stand at the end, we shall have: acetic acid $= C^4O^4H^3,H$; acetate of potash $= C^4O^4H^3,K$; acetate of ammonia, $C^4O^4H^3,H + NH^3$; ammonio-cupric acetate [of which, however, no analysis has come to the author's knowledge], $= C^4O^4H^3,Cu + NH^3$. Here we have 1 At. H replaced by a metal, and in this sense ammonia-salts behave like acids. — Similarly, cacodylic acid $= C^4O^4H^3,H + AsH^3$, the 1 At. H being not yet replaced by a metal; but in the metallic cacodylates, this substitution takes place, and cacodylate of silver, for example, $= C^4O^4H^3,Ag + AsH^3$.

Hence cacodylic acid cannot form any compound with NH^3, the place which the NH^3 should take being already occupied by AsH^3. — Moreover, just as an amidogen-compound, by taking up xHO, may be converted into an ammonia-compound, so likewise in the formation of cacodylic acid, are the arsidogen or cacodyl-compounds converted into an arseniuretted hydrogen compound, and by abstraction of xHO, the contrary transformation may be effected. Thus far, Laurent, whose theory is corroborated by the fact that cacodylic acid exhibits, according to Bunsen, but a very slight acid reaction.

Decompositions. 1. Cacodylic acid heated above 200° is decomposed, with evolution of arsenious acid and stinking arsenical products. — 2. Heated with dry chromic acid, it produces a fiery explosion. — Fuming nitric acid, aqua-regia, and aqueous chromic acid, do not decompose it, even at a boiling heat. — 3. When heated with aqueous phosphorous acid, it immediately gives off the pungent odour of alkarsin, which compound makes the liquid turbid and separates in drops, and at a boiling heat goes off in vapour:

$$C^4AsH^7O^4 + PO^3 = C^4AsH^6O + HO + PO^5$$

(or, according to Gerhardt's formula:

$$C^4AsH^8O^4 + HO + 2PO^3 = C^4AsH^6O + 2PO^5).$$

Hydrogen, phosphuretted hydrogen, arseniuretted hydrogen, sulphurous acid, ammonia, ferrous sulphate, and oxalic acid, have no action upon cacodylic acid. — 4. Perfectly dry hydrochloric acid gas passed over the dry crystals, causes evolution of heat, and forms water, together with a basic perchloride which solidifies in large radiating crystals on cooling. — Dry hydrobromic acid gas passed over well dried cacodylic acid, forms bromide of cacodyl, bromine, and water:

$$C^4AsH^7O^4 + 3HBr = C^4AsH^6Br + 2Br + 4HO$$

(or: $C^4AsH^8O^4 + 5HBr = C^4AsH^6Br + 4Br + 4HO$).

But cacodylic acid distilled with concentrated hydrobromic acid yields basic perbromide of cacodyl. — Dry hydriodic acid gas passed over the dry crystals, causes intense heat, and forms iodide of cacodyl, iodine, and water:

$$C^4AsH^7O^4 + 3HI = C^4AsH^6I + 2I + 4HO;$$

(or: $C^4AsH^8O^4 + 5HI = C^4AsH^6I + 4I + 4HO$).

5. Sulphuretted hydrogen acts upon cacodylic acid, with evolution of heat, both in the dry and in the moist way, forming persulphide of cacodyl, free sulphur, and water; but if the crystallized acid be not well cooled during the passage of the gas, other products are likewise formed, in consequence of the heat evolved:

$$C^4AsH^7O^4 + 3HS = C^4AsH^6S^2 + S + 4HO;$$

(or: $C^4AsH^8O^4 + 4HS = C^4AsH^6S^2 + 2S + 4HO$).

If, however, the cacodylic acid, instead of being dissolved in water, be

dissolved in weak alcohol, the sulphuretted hydrogen forms a large quantity of protosulphide of cacodyl as well as bisulphide:

$$C^4AsH^7O^2 + 3HS = C^4AsH^6S + 2S + 4HO;$$

(or: $C^4AsH^5O^4 + 5HS = C^4AsH^6S + 4S + 4HO$).

6. Cacodylic acid heated with an acid solution of protochloride of tin immediately forms chloride of cacodyl:

$$C^4AsH^7O^4 = 2SnCl + 3HCl = C^4AsH^6Cl + 2SnCl^2 + 4HO;$$

(or: $C^4AsH^5O^4 + 4SnCl + 5HCl = C^4AsH^6Cl + 4SnCl^2 + 4HO$).

7. Aqueous cacodylic acid boiled with zinc yields alkarsin and cacodylate of zinc:

$$3C^4AsH^7O^4 + 2Zn = 2(ZnO,C^4AsH^6O^2) + C^4AsH^6O + 3HO;$$

(or: $5C^4AsH^5O^4 + 4Zn = 4C^4AsH^4ZnO^4 + C^4AsH^6O + 3HO$).

Combinations. Cacodylic acid remains permanent in dry air, but deliquesces in damp air, It dissolves in *Water* in all proportions.

Cacodylates. Cacodylic acid decomposes carbonates when boiled with them. The normal cacodylates contain an atom of metal in place of an atom of hydrogen. The salts are rarely crystalline, more frequently gummy. They require a higher temperature to decompose them than free cacodylic acid; when decomposed, they give off stinking products, and leave a residue of carbonate or arseniate. They are soluble in water and in alcohol. Sulphuretted hydrogen converts them into analogous sulphur-salts in which 4 At. O are replaced by 4 At. S.

Crystallized cacodylic acid does not absorb ammoniacal gas (Laurent).

Cacodylate of Potash. — Crystallizes from the aqueous solution by evaporation in concentric radiated masses, resembling Wavellite; deliquescent.

Cacodylate of Soda. — Similar to the potash-salt, but less deliquescent.

Ferric Cacodylate. — The brown solution produced by boiling the aqueous solution with ferric hydrate, decomposes when evaporated.

Cupric Cacodylate. — The solution of cupric hydrate in the acid leaves a blue gum when evaporated in vacuo; the aqueous solution, when boiled, deposits metallic copper, so very finely divided that it cannot be separated by filtration.

Cupric Cacodylate with Cupric Chloride. — An alcoholic solution of cacodylic acid added in excess to an alcoholic solution of cupric chloride, throws down all the copper in the form of a greenish yellow, gummy precipitate, which, when boiled in the supernatant liquid, becomes granular, and may then be readily washed with absolute alcohol. When heated, it emits vapours which smell of cacodyl and take fire in the air, and leaves cupric chloride, cupric arseniate, arsenic, and charcoal.

Calculation according to Bunsen.				Bunsen.
16 C	96·0	8·99		9·10
4 As	300·0	28·09		
24 H	24·0	2·25		2·13
9 Cu	288·0	26·97		26·94
7 Cl	247·8	23·21		23·12
14 O	112·0	10·49		
$7CuCl + 2(CuO,2C^4AsH^6O^3)[?]$	1067·8	100·00		

Mercuric Cacodylate. — A solution of recently precipitated mercuric oxide in excess of concentrated cacodylic acid yields by spontaneous evaporation, soft, white needles grouped like flocks of wool. These crystals when heated give off mercury, together with stinking products containing alkarsin; they dissolve but partially in water and alcohol, leaving a yellow basic salt.

Cacodylate of Mercuric Chloride. — By mixing the alcoholic solutions of cacodylic acid and corrosive sublimate, pearly scales are obtained, which change to white delicate needles, either by remaining in the liquid or by recrystallization from alcohol. They are inodorous, melt into a transparent, colourless liquid when heated, and are resolved, at a higher temperature, into vapours having an arsenical odour, hydrochloric acid and [di-?] chloride of mercury (*Ann. Pharm.* 46, 40).

Calc. according to Bunsen.			Calc. according to Gm.			Bunsen.
4 C	24·0	5·50	4 C	24·0	5·87	5·89
As	75·0	17·20	As	75·0	18·35	
7 H	7·0	1·60	7 H	7·0	1·71	1·78
3 O	24·0	5·50	4 O	32·0	7·83	
2 Hg	200·0	45·85	2 Hg	200·0	48·92	47·84
3 Cl	106·2	24·35	2 Cl	70·8	17·32	20·54
	436·2	100·00		408·8	100·00	

Bunsen obtained by his calculation, not 24·35, but 21·60 p.c. chlorine, because, from an oversight, he estimated 3 At. Cl, not at 1327·95 (O=100) but at 1106·5. According to Bunsen, the compound is a compound of mercuric oxide with perchloride of cacodyl, $2HgO,C^4AsH^6Cl^3 + HO$; according to Gm. it is cacodylate of mercuric chloride $=2HgCl,C^4AsH^7O^4$.

Cacodylate of Silver. — *a. Monobasic.* A solution of silver-oxide in aqueous cacodylic acid is mixed with excess of silver-oxide and evaporated to dryness, the residue dissolved in hot alcohol, and the filtrate cooled to the crystallizing point. — Long, very delicate needles united in radiated masses, inodorous and permanent in the air. They blacken by exposure to light; may be heated to 100 without decomposition or loss of water; but a temperature a little above 100°, they give off vapours like alkarsin, which take fire in the air, while silver free from arsenic is left behind. Dissolves very readily in water.

Calc. according to Bunsen.			Calc. according to Gerhardt.			Bunsen. *dried at* 100°.
4 C	24	9·79	4 C	24	9·88	9·83
As	75	30·62	As	75	30·86	
6 H	6	2·45	4 H	4	1·64	2·43
AgO	116	47·35	AgO	116	47·74	47·30
3 O	24	9·79	3 O	24	9·88	
$AgO,C^4AsH^5O^3$	245	100·00	$C^4AsH^4AgO^4$	243	100·00	

b. Teracid. — By heating carbonate of silver with aqueous cacodylic acid for several days, evaporating to dryness, and exhausting with water, a salt is obtained of similar character, and crystallizing in needles, but not so readily.

Calc. according to Bunsen.			Calc. according to Gerhardt.			Bunsen. *dried cold in vac.*
12 C	72	13·82	12 C	72	13·98	13·76
2 As	225	43·19	3 As	225	43·69	
20 H	20	3·84	14 H	14	2·72	3·53
AgO	116	22·26	AgO	116	22·52	22·08
11 O	88	16·89	11 O	88	17·09	
	521	100·00	$C^4AsH^4AgO^4,2C^4AsH^5O^4$	515	100·00	

[According to Bunsen, this salt is $AgO,C^4AsH^6O^3 + 2(HO,C^4AsH^6O^3)$; according to Gerhardt, it is $C^4AsH^4AgO^4 + 2C^4AsH^5O^4$. The former calculation gives both in salt *a* and salt *b* more hydrogen than the experiment; and the latter gives much too little H.]

Nitrocacodylate of Silver. — When alcoholic solutions of nitrate and cacodylate of silver are mixed together, large needles separate out, but if left in the liquid, soon change to pearly scales. They must be quickly washed by decantation [with alcohol ?] and dried in the dark over oil of vitriol. — When exposed to light, they very quickly assume a dark brown colour; also when heated 100°, either alone or under water. At 210°, they detonate slightly. They dissolve readily in water, sparingly in absolute alcohol.

Calc. according to Bunsen.			Calc. according to Gerhardt.			Bunsen.
4 C	24	5·78	4 C	24	5·81	6·16
As	75	18·07	As	75	18·16	
6 H	6	1·45	4 H	4	0·97	1·51
3 O	24	5·78	3 O	24	5·81	
2 AgO	232	55·91	2 AgO	232	56·17	55·84
NO^5	54	13·01	NO^5	54	13·08	
	415	100·00		413	100·00	

According to Bunsen, it is $AgO,NO^5 + C^4ArH^4AgO^4$; according to Gerhardt, $AgO,NO^5 + C^4ArH^2AgO^4$.

Cacodylic acid dissolves very readily in very dilute *Alcohol*, less readily in cold absolute alcohol. — It dissolves sparingly in aqueous *Ether*, but not in anhydrous ether, which indeed precipitates it from its alcoholic solution (Bunsen).

Protosulphide of Cacodyl. $C^4AsH^6S = C^4ArH^3,HS$.

BUNSEN. *Ann. Pharm.* 37, 16.

Formed in the decomposition of aqueous cacodylic acid (p. 329) or alkarsin by sulphuretted hydrogen, or of chloride of cacodyl by aqueous hydrosulphate of barium:

$$C^4AsH^6Cl + BaS,HS = C^4AsH^6S + BaCl + HS.$$

The escape of sulphuretted hydrogen causes strong effervescence.

Preparation. 1. When chloride of cacodyl is distilled with aqueous hydrosulphate of barium, protosulphide of cacodyl passes over together with water. As chloride of cacodyl is generally contaminated with alkarsin, which is not acted upon by protosulphide of barium, but is converted into sulphide of cacodyl by the action of hydrosulphate of barium, the latter is better adapted for the preparation than the simple sulphide of barium, which would yield a sulphide of cacodyl containing alkarsin. In the retort there generally remains, besides chloride of barium, a viscid stinking mass consisting of sulphur and a mixture of protosulphide of cacodyl with the bisulphide. For, the hydrosulphate of barium generally contains hyposulphite of baryta and bisulphide of barium; and by the mutual action of these compounds, sulphur is separated, and converts a portion of the protosulphide of cacodyl into bisulphide. If the hydrosulphate of barium contains sulphide of iron, this compound imparts to the sulphide of cacodyl, an indigo-blue colour, which however is removed by distillation. — The distillate thus obtained is once more distilled with hydrosulphate of barium, to convert the chloride of cacodyl completely into sulphide; and the sulphide of cacodyl is then freed from water by means of chloride of calcium, and from sulphuretted hydrogen by carbonate of lead. In these distillations, so long as the sulphide of cacodyl is covered with a layer of water containing sulphuretted hydrogen, no particular care need be taken to exclude the air. because the oxidation-products of the cacodyl are reduced by the sulphuretted hydrogen; but as soon as the sulphide of cacodyl is completely freed from sulphuretted hydrogen, the air must be excluded as carefully as possible. — The sulphide of cacodyl is finally transferred, without being allowed to come in contact with the air, into the distillatory apparatus described on page 321 (*i. e.* a bent glass tube with a bulb at each end), previously filled with carbonic acid, and distilled, whereby any bisulphide of cacodyl that may be present in it, is left behind in the form of a yellowish, viscid, stinking liquid mixed with crystalline grains. — 2. Another mode of preparation is to mix the acid watery layer, which floats on Cadet's crude liquid (p. 316), and contains acetic acid and alkarsin, with aqueous hydrosulphate of barium. The resulting sulphide of cacodyl, which requires further purification, sinks to the bottom, being insoluble in the acid liquid:

$$C^4AsH^6O + C^4H^4O^4 + BaS,HS = C^4AsH^6S + C^4H^3BaO^4 + HO + HS.$$

Properties. Transparent, colourless, ethereal liquid, which does not solidify at — 40°, and is heavier than water. Boils considerably above 100°, but passes over readily with vapour of water. Vapour-density = 7·72. Does not fume in the air. Has an extremely repulsive, penetrating and persistent odour, like mercaptan and alkarsin.

			Bunsen.		Vol.	Density.
4 C	24	19·84	20·49	C-vapour	4	1·6640
As	75	61·98		As-vapour	½	5·1998
6 H	6	4·96	5·02	H-gas	6	0·4158
S	16	13·22	12·17	S-vapour	¼	1·1093
C^4AsH^6S	121	100·00			1	8·3889

Protosulphide of cacodyl, C^4ArH^3,HS, corresponds to hydrosulphuric ether, C^4H^4,HS, and like the latter, yields a monatomic gas.

Decompositions. 1. The vapour heated to redness in a glass bulb, deposits arsenic, sulphide of arsenic, and charcoal. — 2. Sulphide of

cacodyl takes fire readily in contact with air, and burns with a grey arsenical flame, pale blue at the edges. — When exposed to the air or oxygen gas at ordinary temperatures, it is converted into cacodylic acid and bisulphide of cacodyl, which latter may be extracted by ether (*Ann. Pharm.* 46, 4).

$$2C^4AsH^6S + HO + 3O = C^4AsH^7O^4 + C^4AsH^6S^2;$$

(or: $2C^4AsH^6S + 6O = C^4AsH^5O^4 + C^4AsH^5S^2 + 2HO.$

— 3. With iodine it yields a peculiar crystalline substance. — With selenium it forms a compound which crystallizes in large colourless laminæ. The aqueous or alcoholic solution of this compound brought in contact with sulphur, yields bisulphide of cacodyl. — 4. Moderately strong nitric acid oxidizes the sulphur completely, the cacodyl incompletely. — 5. Sulphuric and phosphoric acid eliminate sulphuretted hydrogen and form sulphate or phosphate of cacodyl:

$$C^4AsH^6S + HO,SO^3 = C^4AsH^6O,SO^3 + HS.$$

Acetic acid exerts no decomposing action. — 6. Hydrochloric acid forms chloride of cacodyl and sulphuretted hydrogen:

$$C^4AsH^6S + HCl = C^4AsH^6Cl + HS.$$

7. Protosulphide of cacodyl heated to 200°—300° in a curved receiver over mercury, gives off no gas, but coats the mercury with sulphide of mercury, and is itself converted into a fuming mixture of cacodyl and undecomposed sulphide. At this temperature, however, the cacodyl itself begins to decompose (*Ann. Pharm.* 42, 26).

Combinations. Protosulphide of cacodyl is scarcely soluble in *Water*, but nevertheless imparts to that liquid its own abominable odour.

With the aid of heat, it dissolves *Phosphorus*, which separates out from it again on cooling.

Sulphide of Cacodyl and Copper. $3CuS,C^4AsH^6S$. — Crystallizes from a mixture of the solutions of sulphide of cacodyl and nitrate of copper, in regular octohedrons permanent in the air and having an adamantine lustre (*Ann. Pharm.* 46, 47). — [Alkarsin is probably formed at the same time, as shown by the following equation:

$$4C^4AsH^6S + 3CuO = 3CuS,C^4AsH^6S + 3C^4AsH^6O.]$$

Protosulphide of cacodyl mixes in all proportions with *Ether* and *Alcohol*, and is precipitated from the latter by water (Bunsen).

Bisulphide of Cacodyl. $C^4AsH^6S^2$.

BUNSEN. *Ann. Pharm.* 46, 16.

Persulphide of Cacodyl, Kakodylsulfid.

Formation. 1. Protosulphide of cacodyl, either dry or dissolved in alcohol, is converted, by heating with sulphur, into bisulphide, and by exposure to the air, into a mixture of bisulphide and cacodylic acid

(p. 334). — 2. Sulphuretted hydrogen passed over crystallized cacodylic acid kept cold, or through the aqueous solution of that acid, produces a mixture of bisulphide of cacodyl and sulphur (p. 329).

Preparation. Protosulphide of cacodyl prepared by three distillations with hydrosulphate of barium, and perfectly free from chlorine, is completely freed from water by treating it with chloride of calcium in a flask filled with carbonic acid, then decanted and accurately weighed in a flask likewise filled with carbonic acid, and heated with $\frac{1}{7 \cdot 5 6 4}$ part of well dried flowers of sulphur [16 pts. sulphur to 121 pts. protosulphide of cacodyl]; the sulphur then dissolves, and forms a pale yellow liquid, which on cooling, solidifies completely into a mass consisting of white crystalline scales. As this mass may contain, sometimes a little free sulphur, sometimes a little protosulphide of cacodyl, and likewise traces of cacodylic acid, it is dissolved in absolute alcohol, and alcohol and water added, till the liquid begins at 40° to deposit crystals of bisulphide of cacodyl. Above 40°, the bisulphide would separate in the liquid form, and therefore could not be purified by recrystallization. The mother-liquor is still pure enough for the preparation of sulphocacodylates. 100 pts. protosulphide of cacodyl yield 113·2 pts. of bisulphide. [This agrees very nearly with the calculated amount. 121 : 138 = 100 : 123·2]. — 2. Sulphuretted hydrogen gas is passed through aqueous cacodylic acid; the precipitated mixture of free sulphur and bisulphide of cacodyl treated with hot dilute alcohol, to extract the latter; and the liquid filtered, and left to cool to the crystallizing point.

Properties. Bisulphide of cacodyl crystallizes from the alcoholic solution by slow cooling in large transparent, colourless tables: by quicker cooling, in small prisms. The crystals are soft and greasy to the touch. They melt at 50° to a colourless liquid, which, on cooling, solidifies in a crystalline laminated mass. Has a penetrating odour, like that of *asa fœtida*. Permanent in the air.

			Bunsen.
4 C	24	17·52	17·38
As	75	54 74	54·96
6 H	6	4·38	4·31
2 S	32	23·36	23·38
$C^4AsH^6S^2$	137	100·00	100·03

Bunsen assigns to the compound the rational formula $C^4AsH^5S, C^4AsH^6S^3$. According to the nucleus-theory also, a peculiar formula would be required for this compound, inasmuch as it contains an uneven number of atoms.

Decompositions. 1. Bisulphide of cacodyl, heated above its boiling-point, assumes a yellowish colour, gives off protosulphide of cacodyl, together with a little undecomposed bisulphide, and leaves a mixture of sulphur and the bisulphide separable by alcohol; at a higher temperature, protosulphide of cacodyl distils over, together with a small quantity of bisulphide, and sulphur sublimes together with a trace of sulphide of arsenic; lastly, at a red heat, sulphide of arsenic is formed, together with a number of stinking products of decomposition. — 2. Bisulphide of cacodyl heated in the air, burns with a dull bluish flame, forming water, carbonic acid, sulphurous acid, and arsenious acid, which rises in the form of a

white smoke. — 3. Nitric acid converts it into sulphur which separates, and sulphuric and cacodylic acid:

$$C^4AsH^6S^2 + HO + NO^5 + C^4AsH^7O^4 + 2S + NO^2.$$

4. It dissolves in oil of vitriol, with evolution of sulphurous acid and abundant separation of sulphur. — 5. It is decomposed by peroxide of lead, yielding cacodylate of lead, sulphide of lead, and sulphur:

$$2C^4AsH^6S^2 + 4PbO^2 = 2(PbO,C^4AsH^6O^3) + 2PbS + 2S.$$

[If cacodylic acid were $=C^4AsH^5O^4$, there ought to be no separation of sulphur in the free state, since the equation would be:

$$C^4AsH^6S^2 + 3PbO^2 = C^4AsH^4PbO^4 + 2PbS + 2HO.]$$

6. From many heavy metallic salts, bisulphide of cacodyl throws down a sulphocacodylate. [Probably with simultaneous formation of alkarsin: *e. g.* with a lead-salt:

$$2C^4AsH^6S^2 + PbO = C^4AsH^6PbS^4 + C^4AsH^6O.]$$

7. With mercury it forms, even at ordinary temperatures, and with great evolution of heat, sulphide of mercury and sulphide of cacodyl, which then, on being heated to 200°, is converted, with further formation of sulphide of mercury, into cacodyl.

Combinations. Bisulphide of cacodyl is insoluble in water.

It dissolves in *Hydrochloric acid*, and apparently without decomposition.

It dissolves sparingly in *Ether*, but readily in *Alcohol* both hydrated and absolute. From this latter, it separates, on dilution with water to a certain extent, in oily drops, which when left at rest, remain liquid, even at +20°, but on the slightest movement, solidify in fine crystals, and with great evolution of heat (Bunsen).

Bunsen succeeded but imperfectly in preparing a *Persulphide of Cacodyl* $=C^4AsH^6S^3$, in the separate state. A fused mixture of 1 At. protosulphide of cacodyl and 2 At. sulphur solidifies on cooling, in a crystalline mass consisting of scales, and differing from the bisulphide of cacodyl obtained in a similar manner and crystallized from alcohol. But when the crystals are treated with hot absolute alcohol, sulphur remains behind, amounting to less than 1 At., and the alcohol, on cooling, yields, together with free sulphur and crystals of bisulphide of cacodyl, a few separate crystals, differing in form from those of the bisulphide, and containing more sulphur than that compound.

Sulphocacodylates. $MS,C^4AsH^6S^3=C^4AsH^6MS^4$.

BUNSEN. *Ann. Pharm.* 46, 23.

As Bunsen assigns to these salts the formula $MS,C^4AsH^6S^3$, he assumes the existence of a sulphocacodylic acid, or persulphide of cacodyl, $C^4AsH^6S^3$, corresponding to the hypothetical anhydrous cacodylic acid, $C^4AsH^6O^3$. The nucleus-theory, on the other hand, supposes the existence of a sulphur acid $= C^4AsH^7S^4$ (or, according to Gerhardt, $C^4AsH^5S^4$) corresponding to crystallized cacodylic acid, and forming the sulphocacodylates by substitution of 1 At. metal for 1 At. hydrogen. In the case of antimony and bismuth, which form teracid oxides, the radical-theory

supposes that 1 At. of a metallic sulphide unites with 3 At. of the sulphur-acid $C^4AsH^6S^3$, while, according to the nucleus-theory, 1 At. of these metals replaces 3 At. hydrogen in 3 At. of the sulphur-acid $C^4AsH^7S^4$.

Formation. 1. By bringing various heavy metallic salts dissolved in alcohol, in contact with bisulphide of cacodyl (p. 336). — 2. By decomposing a heavy metallic cacodylate with hydrosulphuric acid (p. 320).

Sulphocacodylate of Antimony. — A mixture of the concentrated alcoholic solutions of bisulphide of cacodyl and terchloride of antimony (containing excess of hydrochloric acid) deposits short, flat, light yellow needles, which however cannot be completely freed from chlorine by alcohol, and are therefore perhaps mixed with a chlorine-compound. — If the alcoholic solutions are dilute and do not contain excess of hydrochloric acid, they form a yellowish white precipitate which after a time assumes a yellow and then an orange colour, arising from precipitated sulphide of antimony; this decomposition likewise takes place when the product is washed with alcohol.

	Crystals.			Bunsen.
12 C	72	....	11·32	..... 11·88
3 As	225	....	35·38	
18 H	18	....	2·83	..... 3·00
Sb	129	....	20·28	
12 S	192	....	30·19	
$SbS^3,3C^4AsH^6S^3 = C^{12}As^3H^{18}SbS^{12}$	636	....	100·00	

Sulphocacodylate of Bismuth. — Formed by adding a dilute boiling alcoholic solution of acid nitrate of bismuth, by drops and with constant stirring, to a boiling concentrated alcoholic solution of bisulphide of cacodyl. The mixture assumes a golden yellow colour, and deposits after a few minutes, soft, bulky, woolly needles which soon change to crystalline scales. The mother-liquor, which still contains bisulphide of cacodyl, may be decanted, and the bismuth-solution again dropped in several times with the same precautions, till on further addition, the first traces of a black precipitate of sulphide of bismuth make their appearance.

Delicate, golden yellow, inodorous scales which are permanent in the air. They sustain a heat of 100° without alteration, but at a higher temperature, are resolved into sulphide of bismuth, sulphide of cacodyl and sulphur. They are not altered by sulphuretted hydrogen. They are insoluble in water and nearly insoluble in alcohol and ether.

	Crystals.			Bunsen.
12 C	72	....	10·00	..... 10·02
3 As	225	....	31·25	
18 H	18	....	2·50	..... 2·56
Bi	213	....	29·58	..... 30·13
12 S	192	....	26·67	
$BiS^3,3C^4AsH^6S^3 = C^{12}As^3H^{18}BiS^{12}$	720	....	100·00	

Sulphocacodylate of Lead. — By mixing the alcoholic solutions of bisulphide of cacodyl and acetate of lead, small white, pearly scales are obtained, which are inodorous and permanent in the air, not affected by sulphuretted hydrogen, insoluble in water, and nearly insoluble in alcohol.

	Crystals.			Bunsen.
4 C	24	....	8·79	..... 8·95
As	75	....	27·47	
6 H	6	....	2·20	..... 2·28
Pb	104	....	38·10	
4 S	64	....	23·44	
$PbS,C^4AsH^6S^3 = C^4AsH^6PbS^4$	273	....	100·00	

Sulphocacodylate of Copper. — An alcoholic solution of nitrate of copper is added to an alcoholic solution of bisulphide of cacodyl, in such proportion that the latter may greatly predominate, and the precipitate washed with absolute alcohol (Bunsen):

$$4C^4AsH^6S^2 + 4(CuO,NO^5) + HO = 2(Cu^2S,C^4AsH^6S^3) + C^4AsH^7O^4 + C^4AsH^6O,NO^5 + 4NO^5.$$

If too much nitrate of copper be added, sulphide of copper is precipitated, together with a peculiar sulphur-salt which crystallizes in long needles, and decomposes spontaneously after a while, with formation of sulphide of copper.

Soft, loose, egg-yellow powder, which takes up water but slowly. When heated, it first gives off sulphide of cacodyl, then sulphur, and leaves sulphide of copper. It is decomposed by potash, but not by sulphuretted hydrogen. It is insoluble in water, aqueous acids, alcohol and ether.

				Bunsen.
4 C	24	....	10·30	..... 10·4
As	75	....	32·19	..... 31·5
6 H	6	....	2·57	..... 2·5
2 Cu	64	....	27·47	..... 27·1
4 S	64	....	27·47	..... 28·5
$Cu^2S,C^4AsH^6S^3$	233	....	100·00	..... 100·0

Sulphocacodylate of Gold. — The alcoholic solutions of bisulphide of cacodyl and terchloride of gold form a brown precipitate of sulphide of gold, which, when boiled for some time with the supernatant liquid, is converted into a yellowish grey-white sandy powder, sinking quickly to the bottom; it must be washed with absolute alcohol and dried in vacuo. The filtrate contains cacodylic acid:

$$2C^4AsH^6S^2 + AuO^3 + HO = C^4AsH^6AuS^4 + C^4AsH^7O^4.$$

This compound, when dry, forms a very soft, yellowish white, tasteless and inodorous powder, which appears perfectly homogeneous when examined by the microscope. When heated, it assumes a dark-red colour, and gives off nearly pure sulphide of cacodyl in oily drops, and afterwards sulphur, while pure gold remains behind. It is set on fire by fuming nitric acid, with separation of sulphur and gold. It is decomposed by caustic potash, but not by sulphuretted hydrogen. Insoluble in water, hydrochloric acid, alcohol and ether.

				Bunsen.
4 C	24	....	6·52	..... 6·61
As	75	....	20·38	
6 H	6	....	1·63	..... 1·76
Au	199	....	54·08	..... 53·73
4 S	64	....	17·39	..... 17·75
$C^4AsH^6AuS^4$	368	....	100·00	

Selenide of Cacodyl. $C^4AsH^6Se=C^4ArH^3,HSe$.

BUNSEN. *Ann. Pharm.* 37, 21.

Formed by distilling pure chloride of cacodyl two or three times with aqueous selenide of sodium, and purifying the oily distillate at the bottom of the water, in the same manner as the sulphide (p. 333).

Transparent, yellow oil, heavier than water. Does not fume in the air, and has a peculiarly high boiling point, but may be distilled without decomposition either alone or with water. Has a repulsive, extremely penetrating, and somewhat ethereal and aromatic odour.

The vapour of selenide of cacodyl passed through a red-hot glass tube, deposits a ring of selenium and arsenic. Selenide of cacodyl exposed to the air, takes up oxygen and forms colourless crystals; when set on fire, it burns with a beautiful blue flame, emitting a strong odour of selenium. It is readily oxidized by nitric acid; also by heated oil of vitriol, with evolution of sulphurous acid and precipitation of red selenium. From various heavy metallic salts, as from acetate of lead or nitrate of silver, it throws down a black metallic selenide, while alkarsin remains dissolved in combination with the acid:

$$C^4AsH^6Se + AgO,NO^5 = C^4AsH^6O,NO^5 + AgSe.$$

On the addition of a small quantity of corrosive sublimate, it forms a black precipitate of selenide of mercury; then, on further addition, a white precipitate, consisting of a compound of alkarsin with protochloride of mercury, which may be extracted by boiling water, and crystallizes from the solution in nacreous laminæ:

$$C^4AsH^6Se + 3HgCl + HO = HgSe + C^4AsH^6O,2HgCl + HCl.$$

Selenide of cacodyl is insoluble in water, but dissolves readily in *Alcohol* and *Ether* (Bunsen).

Iodide of Cacodyl. $C^4AsH^6I=C^4ArH^3,HI$.

BUNSEN. *Ann. Pharm.* 37, 35.

1. When alkarsin is distilled with concentrated hydriodic acid, a yellowish oil collects under the water in the receiver, which, on cooling, deposits yellowish crusts and transparent rhombic tables of oxyiodide of cacodyl. After this separation has been more completely effected, by surrounding the receiver with a frigorific mixture, the oily iodide of cacodyl is poured off; again distilled with concentrated hydriodic acid; set aside for a few days with chloride of calcium and quicklime in a sealed tube filled with carbonic acid gas, to remove water and hydriodic acid; and finally distilled in apparatus 3 (p. 321), previously filled with carbonic acid gas and sealed, till $\frac{1}{2}$ to $\frac{2}{3}$ has passed over. — The watery distillate in the receiver, which has been converted into ice by the freezing mixture, yields, when separated from the oxyiodide and thawed, an additional quantity of iodide of cacodyl, but less pure (Bunsen). — ¶ 2. Iodide of cacodyl is also formed, together with the iodide of

another arsenical radical, by the action of iodide of methyl, ethyl, amyl, &c., on cacodyl:

$$2C^nH^{n+1}I + 2C^4H^6As = (C^2H^2)^2(C^nH^{n+1})^2As,I + C^4H^6AsI.$$

e.g. with iodide of ethyl, the products are iodide of arsenmethylethylium and iodide of cacodyl (Cahours & Riche, pp.319, 352). ¶

Thin yellowish distillate, which does not solidify at — 10°; it is heavier than chloride of calcium, but lighter than lime. Boils above 100°, forming a yellow vapour; may be readily distilled with water; does not fume in the air; has a penetrating and repulsive odour like that of cacodyl.

			Bunsen.
4 C	24	10·39	10·60
As	75	32·47	31·47
6 H	6	2·60	2·60
I	126	54·54	55·25
C^4AsH^6I	231	100·00	99·92

Iodide of cacodyl set on fire in the air, burns with a light smoky flame, giving off vapours of iodine. Exposed to the air at ordinary temperatures, it forms in a short time, beautiful rhombic prisms, probably consisting of cacodylic acid. It is decomposed by nitric and sulphuric acid, with separation of iodine. With protochloride of mercury, it behaves like the corresponding compounds. Mercury abstracts the iodine, even below the boiling point of the compound.

It is insoluble in water, but dissolves in *Alcohol* and *Ether* (Bunsen).

Oxyiodide or Basic Iodide of Cacodyl.

Probably = $3C^4AsH^6I,C^4AsH^6O$.

Bunsen. *Ann. Pharm.* 37, 54.

Formation and Preparation. 1. Passes over, together with iodide of cacodyl, in the distillation of alkarsin with concentrated hydriodic acid (p. 339). To free the crystals from the oily iodide which still adheres to them, they are several times pressed between paper; recrystallized from boiling absolute alcohol; freed from adhering alcohol by pressure under water: left for some days in contact with fragments of chloride of calcium; and distilled in apparatus 3 (p. 321), previously filled with carbonic acid, till half the product has passed over. This compound oxidizes so rapidly in the air, that it cannot be obtained quite free from oxidation-products. — 2. The same compound is formed by mixing alkarsin with iodide of cacodyl — these bodies combining in all proportions — and adding a very small quantity of water, which immediately converts the fluid mixture into a yellow crystalline mass. — On the other hand, the compound is not obtained by digesting or distilling iodide of cacodyl with concentrated hydriodic acid.

Yellow crystalline mass or transparent rhombic tables. Melts far below 100°, and may be distilled without decomposition. Emits white fumes in the air.

Absorbs oxygen from the air so rapidly, that it becomes heated to its

melting point, and even takes fire. Burns with a smoky flame, giving off vapours of iodine. Not converted into iodide of cacodyl, either by digestion or distillation with hydriodic acid.

Dissolves sparingly in water, very readily in alcohol (Bunsen).

Bromide of Cacodyl. Probably = $C^4AsH^6Br = C^4ArH^3,HBr$.

BUNSEN. *Ann. Pharm.* 37, 38; 42, 26.

By distilling the compound of alkarsin and mercuric chloride with highly concentrated hydrobromic acid, a yellow, non-fuming distillate is obtained, having the properties of chloride of cacodyl (Bunsen). — This compound is also formed by the action of bromide of ethyl on cacodyl (Cahours & Riche, p. 352). Bromide of cacodyl placed over mercury in a curved receiver, and heated to 200° — 300°, is converted, with formation of mercurous bromide, into a mixture of cacodyl and bromide of cacodyl, which fumes strongly, and even takes fire spontaneously on exposure to the air; but on boiling with water, the mercurous bromide is reduced to the metallic state, and the cacodyl reconverted into bromide which volatilizes with the watery vapours. — When heated with water, it is converted into fuming oxybromide of cacodyl (Bunsen).

Oxybromide or Basic Bromide of Cacodyl.

$3C^4AsH^6Br,C^4AsH^6O$.

BUNSEN. *Ann. Pharm.* 37, 52.

Obtained by distilling alkarsin two or three times with moderately strong hydrobromic acid; rectifying the resulting distillate with chalk-powder and water, the air being completely excluded; then drying it over chloride of calcium, and distilling it once more in the distillatory apparatus (3), (p. 321), filled with carbonic acid gas.

Yellow liquid becoming colourless whenever it is heated; in other respects very much like bromide of cacodyl.

When heated with mercury, it is converted, without evolution of gas, into a lemon-yellow, easily fusible substance, which may be evaporated without decomposition, but when more strongly heated alone, is resolved into mercury, mercurous bromide, and stinking arseniferous products, and when heated with water, yields mercury and a compound which volatilizes with the water (Bunsen).

			Bunsen.
16 C	96	14·37	14·60
4 As	300	44·91	45·15
24 H	24	3·59	3·61
3 Br	240	35·93	34·60
O	8	1·20	2·04
$3C^4AsH^6Br,C^4AsH^6O$	668	100·00	100·00

Basic Perbromide of Cacodyl.

BUNSEN. *Ann. Pharm.* 46, 41.

Cacodylic acid is dissolved in very strong hydrobromic acid, in such quantity that the solution may still exhibit a strong acid reaction, and the liquid evaporated in vacuo over oil of vitriol and lime. Basic perbromide of cacodyl then remains, and is the only product. If the hydrobromic acid has been prepared from bromine and sulphuretted hydrogen, it will contain sulphuric acid, which must be precipitated by baryta-water. Water must then be distilled off from the aqueous hydrobromic acid till the distillate begins to exhibit an acid reaction, and the residue becomes yellowish from the presence of free bromine. Lastly, this residue distilled with phosphatic acid yields hydrobromic acid, colourless and sufficiently concentrated for the purpose.

Viscid, colourless, inodorous syrup, which does not redden litmus-paper, excepting on addition of water.

a. Calc. accord. to Bunsen.			*b*. Calc. accord. to Gm.			Bunsen.
16 C	96	11·43	24 C	144	12·31	11·78
4 As	300	35·71	6 As	450	38·46	
36 H	36	4·29	48 H	48	4·10	4·38
3 Br	240	28·57	4 Br	320	27·35	26·44
21 O	168	20·00	26 O	208	17·78	
	840	100·00		1170	100·00	

According to Bunsen, this compound $= C^4AsH^6Br^3, 3C^4AsH^6O^3 + 12Aq$; according to Gm., $= C^4AsH^7Br^4, 5C^4AsH^7O^4 + 6Aq$; according to this latter formula, the formation of the compound must be expressed by the following equation:

$$6C^4AsH^7O^4 + 4HBr + 2HO = C^4AsH^7Br^4, 5C^4AsH^7O^4 + 6HO.$$

Moreover, since the quantity of cacodylic acid to be dissolved in the hydrobromic acid is not very exactly determined, the mixture may contain variable quantities of cacodylic acid and of the corresponding bromo-acid, C^4AsH^7Br. Bunsen appears to conclude, chiefly from the circumstance that the compound does not redden litmus while in the syrupy state, but only after dilution with water, that the syrup no longer contains any acid, but is reconverted into an acid by the water; but this want of action upon litmus may arise from the thick consistency of the syrup, or from the same cause as that which renders tartaric acid dissolved in absolute alcohol incapable of reddening litmus.

The compound, when moderately heated, is resolved into water, gaseous bromide of methyl (VII, 286) cacodylate of cacodylic bromide, and arsenious acid (*Ann. Pharm.* 46, 44). [The equation given by Bunsen for this decomposition cannot be correct. — Respecting cacodylate of cacodylic bromide, nothing further is mentioned. — If we start from the formula *b*, the equation will be:

$$C^4AsH^7Br + 5C^4AsH^7O^4 + 6HO = 9HO + 2C^2H^3Br + 2C^4AsH^6Br + 3C^4AsH^7O^4 + AsO^5.$$

According to this equation, water, bromide of methyl, bromide of cacodyl, cacodylic acid, and *arsenic acid* would be obtained]. The compound, when dissolved in water, is resolved into cacodylic acid and hydrobromic acid, which volatilizes, together with the water, when the liquid is evaporated in vacuo (Bunsen). [Equation according to formula *b*:

$$C^{24}As^6H^{48}Br^4O^{26} = 6C^4AsH^7O^4 + 4HBr + 2HO].$$

Chloride of Cacodyl. $C^4AsH^6Cl = C^4ArH^3,HCl$.

BUNSEN. *Ann Pharm.* 37, 31.

Preparation. 1. The compound of alkarsin with protochloride of mercury, is distilled with very strong hydrochloric acid, and the distillate dried apart from the air, over chloride of calcium and magnesia, and distilled alone in the apparatus described on page 321, previously filled with carbonic acid gas and sealed. — Alkarsin, distilled with strong hydrochloric acid, does not yield chloride of cacodyl in a state of purity, because oxychloride of cacodyl is formed at the same time, and is not decomposed, even by repeated distillation with hydrochloric acid (Bunsen). — Chloride of cacodyl is also obtained by the action of chloride of ethyl on cacodyl (Cahours & Riche, p. 353).

Properties. Transparent, colourless, ethereal liquid, which does not solidify even at — 45°; heavier than water. Boils a little above 100°, and forms a colourless vapour of sp. gr. 4·56. Does not fume in the air, Has a penetrating, intoxicating odour, much more powerful than that of alkarsin; when inhaled in considerable quantity, it produces swelling of the mucous membrane of the nose, and extravasation of blood in the eyes.

			Bunsen.		Vol.	Density.
4 C	24·0	17·09	17·70	C-vapour	4	1·6640
As	75·0	53·42		As-vapour	½	5·1998
6 H	6·0	4·27	4·35	H-gas	6	0·4158
Cl	35·4	25·22	22·90	Cl-gas	1	2·4543
C^4AsH^6Cl	140·4	100·00		Vapour of C^4AsH^6Cl	2	9·7339
					1	4·8669

In consequence of the admixture of oxychloride of cacodyl, Bunsen found too little chlorine.

Decompositions. 1. Chloride of cacodyl, when set on fire, burns with a dull arsenic flame, depositing metallic arsenic or arsenious acid, according to the facility with which the air has access to it. The vapour which it evolves on boiling, takes fire spontaneously in the air. When heated in a vessel filled with oxygen, it explodes with great violence. — When the air has excess to it but sparingly, it deposits crystals. — 2. In chlorine gas, it takes fire spontaneously, and deposits charcoal. — 3. Strong nitric acid sets fire to it, with explosion. — 4. It is decomposed, with evolution of hydrochloric acid, by sulphuric and phosphoric acid, but not by weaker acids. — 5. With dry ammoniacal gas, it forms a white saline mass, which leaves sal-ammoniac when treated with alcohol. — 6. Alcoholic potash reduces it to the arsidogen-nucleus C^4AsH^5 (p. 316), with precipitation of chloride of potassium:

$$C^4AsH^6Cl + KO = C^4AsH^5 + KCl + HO.$$

Dry baryta or lime does not abstract chlorine from it; even from the vapour, heated lime does not withdraw the chlorine till the heat becomes

sufficiently great to decompose the chloride of cacodyl without the intervention of any other substance. — 7. Silver-salts decompose chloride of cacodyl, throwing down all the chlorine in the form of chloride of silver. — Zinc, tin, and iron abstract all the chlorine, without evolution of gas, and leave cacodyl. Zinc and tin produce this effect at 90° to 100°; the liquid, which at first is transparent and colourless, becomes dark and opaque as the metal dissolves, and on cooling solidifies in a moist saline mass, from which water dissolves out the metallic chloride (*Ann. Pharm.* 42, 27).

Combinations. Chloride of cacodyl is not perceptibly soluble in water, but nevertheless imparts its penetrating odour to that liquid.

With metallic chlorides it forms many compounds; none of which, however, are stable, excepting the following:

Cacodylo-cuprous Chloride. — An alcoholic solution of alkarsin forms, with a solution of cuprous chloride in hydrochloric acid, a thick white pasty precipitate, which must be triturated for some time in a mortar with strong hydrochloric acid, to remove all the cuprous chloride precipitated in the free state; then washed as quickly as possible and quite apart from the air, first with strong, then with dilute hydrochloric acid, and afterwards with water; then pressed between paper and dried in vacuo. If the washing be too long continued, the precipitate is decomposed, and in the end dissolves completely. — White granular powder smelling of cacodyl; often, however, yellowish from incipient decomposition. — When heated, it gives off chloride of cacodyl, and leaves cuprous chloride. When exposed to the air, it turns green, forming chloride of copper and stinking arsenical products. Decomposed by boiling with water. Insoluble in alcohol and in ether (*Ann. Pharm.* 42, 22).

					Bunsen.
4 C	24·0	....	10·01	.....	9·68
As	75·0	....	31·28		
6 H.	6·0	....	2·50	.....	2·62
Cl	35·4	....	14·76	.....	12·44
Cu^2Cl	99·4	....	41·45	.....	40·49
Cu^2Cl,C^4AsH^6Cl	239·8	....	100·00		

Cacodylo-platinic Chloride. — Chloride of cacodyl forms with solution of platinum, a copious brick-red precipitate, probably consisting of $PtCl^2,C^4AsH^6Cl$. — This precipitate dissolves in water when boiled or washed with it, forming a nearly colourless liquid, in which neither platinum nor cacodyl can be detected by the ordinary re-agents; when cooled or evaporated, it yields long colourless needles. These needles are analogous to Reiset's platinum-compounds, the ammonium being replaced by cacodyl. They contain a platiniferous radical, which unites with chlorine, bromine and cyanogen, and forms with oxygen a base which unites with acids, forming crystallized salts (Bunsen).

Oxychloride or Basic Chloride of Cacodyl.

$3C^4AsH^6Cl,C^4AsH^6O$.

BUNSEN. *Ann. Pharm*, 37, 49.

Obtained by treating chloride of cacodyl with water, or more readily, by distilling alkarsin with dilute hydrochloric acid, rectifying the distillate with chalk powder and water — always carefully excluding the air — drying the rectificate over chloride of calcium, and again distilling it in the apparatus described on page 321, previously filled with carbonic acid and sealed.

The liquid resembles chloride of cacodyl, but boils at 109°, has a vapour-density of 5·46, and emits white fumes in the air; its odour is not near so strong as that of alkarsin, but nevertheless quite bad enough.

			Bunsen.			Vol.	Density.
16 C	96·0	17·97	17·74	C-vapour	16	6·6560
4 As	300·0	56·16	55·15	As-vapour	2	20·7994
24 H	24·0	4·49	4·31	H-gas	24	1·6640
3 Cl	106·2	19·88	18·78	Cl-gas	3	7·3629
O	8·0	1·50	4·02	O-gas	½	0·5546
$3C^4AsH^6Cl,C^4AsH^6O$	534·2	100·00	100·00		8	37·0369
					1	4·6296

In consequence of the rapid oxidation of the preparation in the air, which cannot be altogether prevented, Bunsen obtained too much oxygen. [Bunsen's calculation of the vapour-density is inadmissible; for, he reckons 1 vapour-density of alkarsin to 3 vapour-densities of chloride of cacodyl, and by dividing by 4 obtains the vapour-density of the compound = 5·35, which certainly agrees better with the density found by experiment. Since, however, the vapour of alkarsin is monatomic, and that of chloride of cacodyl diatomic, it follows that in the vapour of the oxychloride, 1 vol. alkarsin-vapour must be associated, not with three, but with six volumes of vapour of chloride of cacodyl].

Hydrated Chloride of Cacodyl [?].

BUNSEN. *Ann. Pharm.* 37, 54.

Hydrochloric acid gas dried by oil of vitriol and chloride of calcium, and passed over pure alkarsin, from which the air is carefully excluded, is quickly absorbed, with great evolution of heat, rising even to the boiling point, and forms two strata of liquid, a brick-red powder of erythrarsin (amounting to ½ p.c. of the alkarsin used) being at the same time precipitated. If the alkarsin be surrounded with a frigorific mixture during the passage of the gas, a homogeneous liquid is obtained, which, however, when heated in a distillatory apparatus filled with carbonic acid, till it ceases to give off hydrochloric acid gas (which carries watery vapour with it) is likewise resolved into two strata of liquid, part distilling over.

The thin upper layer is chloride of cacodyl. The lower viscid layer must, since nothing else is formed, be chloride of cacodyl in combination with part of the water which was produced in the formation of that

compound. In fact, chloride of calcium deliquesces in it, leaving chloride of cacodyl almost chemically pure (Bunsen). [Was the substance which caused the deliquescence of the chloride of calcium, really water? Why is not the viscid compound formed on bringing chloride of cacodyl in contact with a small quantity of water?].

Cacodylate of Cacodylic Chloride [?].

BUNSEN. *Ann. Pharm.* 46, 36.

Passes over as an oil in the distillation of basic perchloride of cacodyl. It is rectified at a gentle heat till the residue begins to be somewhat coloured, then freed from water and hydrochloric acid by means of baryta, and distilled once more in the sealed apparatus (p. 321).

The oil resembles chloride of cacodyl. If a glass rod moistened with it be held near the nose for only a few seconds, the odour, which is at first scarcely perceptible, rises after a while to an incredible intensity, causing sneezing, profuse discharge of mucus, and reddening of the nose and eyes. If it be smelt somewhat longer, the odour passes into an intolerable sensation, attended with piercing pain in the cerebellum. — This compound forms, with corrosive sublimate, the same pearly scales as alkarsin (p. 324), but without formation of calomel (Bunsen).

	Calculation, according to Bunsen.			Bunsen.
20 C	120·0	....	15·28	14·90
5 As	375·0	....	47·75	45·65
30 H	30·0	....	3·82	3·81
6 Cl	212·4	....	27·04	26·21
6 O	48·0	....	6·11	9·43
	785·4	....	100 00	100·00

Bunsen attributes the excess of oxygen which he found, to rapid oxidation in the air, and gives the formula $3C^4AsH^6Cl^2,2C^4AsH^6O^3$.

Perchloride of Cacodyl [?].

BUNSEN. *Ann. Pharm.* 46, 29.

Dry hydrochloric acid gas passed over dry cacodylic acid, evolves great heat, and forms a liquid, which on cooling deposits large shining laminæ of basic perchloride of cacodyl. The mother-liquor, which still contains some of this compound, must be regarded as perchloride of cacodyl: in fact, as $C^4AsH^6Cl^3$, inasmuch as, when the hydrochloric acid gas is passed over the cacodylic acid, no separation of water takes place till the gas is in excess, and thereby exerts a decomposing action on the compound already formed. [The compound may also be $C^4AsH^7Cl^4,4HO$, according to the following equation:

$$C^4AsH^7O^4 + 4HCl = C^4AsH^7Cl^4 + 4HO.]$$

The compound is a transparent, colourless, inodorous syrup, which slightly in the air.

syrup when strongly heated, is resolved, without turning brown,

into a volatile product containing chloride of cacodyl, and into arsenious acid and a permanent gas, which is absorbed by alcohol, but not by water. It cannot be set on fire without bringing it into an alcohol flame. Zinc reduces it, even in the cold, to chloride of cacodyl, recognizable by its odour, and at higher temperatures to cacodyl. The aqueous solution of the syrup contains hydrochloric and cacodylic acid, besides a trace of arsenious acid (proceeding from admixed basic perchloride of cacodyl) (Bunsen).

Basic Perchloride of Cacodyl.

BUNSEN. *Ann. Pharm.* 46, 30.

Produced by the action of gaseous or concentrated aqueous hydrochloric acid upon cacodylic acid.

Preparation. 1. By collecting the shining laminæ which separate in the preparation of perchloride of cacodyl. — 2. By evaporating the solution of anhydrous cacodylic acid in highly concentrated hydrochloric acid, over oil of vitriol and lime in vacuo at ordinary temperatures, till it solidifies to a pasty mass made up of laminæ; pressing this mass in a heated press between several folds of warm and well dried bibulous paper; exposing the residue several times to the air to absorb moisture; again pressing it out; and lastly drying it in vacuo over oil of vitriol and lime.

Properties. Large, transparent, colourless, crystalline laminæ, which fuse somewhat below 100°, forming a colourless liquid; they are inodorous, but have a very sour taste.

Calc. according to Bunsen.			Calc. according to Gm.			Bunsen
12 C	72·0	13·76	16 C	96·0	14·51	13·85
3 As	225·0	43·00	4 As	300·0	45·34	
24 H	24·0	4·59	28 H	28·0	4·24	4·61
3 Cl	106·2	20·30	4 Cl	141·6	21·40	20·12
12 O	96·0	18·35	12 O	96·0	14·51	
	523·2	100·00		661·6	100·00	

According to Bunsen, the compound = $C^4AsH^6Cl^3,2C^4AsH^6O^3 + 6HO$; according to Gm., = $C^4AsH^7Cl^4,3C^4AsH^7O^4$. According to the latter formula, the equation for the formation of the compound is:

$$4C^4AsH^7O^4 + 4HCl = C^{16}As^4H^{28}Cl^4O^{12} + 4HO.$$

Basic perchloride of cacodyl begins to decompose even below its melting point, not turning brown, but giving off a permanent gas. Hence a certain amount of decomposition takes place in passing hydrochloric acid gas over cacodylic acid without cooling. If a solution of cacodylic acid in concentrated hydrochloric acid be evaporated to a syrup, and gently heated (between 100° and 109° decomposition takes place more quickly), gaseous chloride of methyl is obtained, which, when purified by passing through water, potash-ley, and hydrate of potash, amounts to 25 cub. centim. for 1 grm. of cacodylic acid; also an oily distillate, consisting of cacodylate of cacodylic chloride, with small quantities of wate and hydrochloric acid; and a residue of arsenious acid, generally mix

with cacodylate of cacodylic chloride and undecomposed basic perchloride of cacodyl. [The equation given for this decomposition by Bunsen (*Ann. Pharm.* 46, 38) is incorrect]. — Basic perchloride of cacodyl deliquesces quickly in the air to a viscid liquid, and its aqueous solution contains nothing but cacodylic and hydrochloric acid:

$$C^{12}As^3H^{24}Cl^3O^{12} = 3C^4AsH^7O^4 + 3HCl,$$

[or: $C^{16}As^4H^{28}Cl^4O^{12} + 4HO = 4C^4AsH^7O^4 + 4HCl$.]

With zinc it yields cacodylic acid, cacodyl and chloride of zinc:

$$C^{12}As^3H^{24}Cl^3O^{12} + 3Zn = 2C^4AsH^7O^4 + C^4AsH^6 + 3ZnCl + 4HO,$$

[or: $C^{16}As^4H^{28}Cl^4O^{12} + 4Zn = 3C^4AsH^7O^4 + C^4AsH^6 + 4ZnCl + H$;

according to this equation, 1 At. H should be set free as gas; whether any evolution of gas takes place or not, Bunsen does not state].

Fluoride of Cacodyl.

BUNSEN. *Ann. Pharm.* 37, 38.

By distilling the compound of alkarsin and mercuric chloride with concentrated hydrofluoric acid, a colourless liquid is obtained, having an intolerably pungent and offensive odour. This liquid is probably = C^4AsH^6F; but, as it attacks glass, it could, perhaps, only be obtained pure by preparing it in platinum vessels. It is insoluble in water, but appears to be decomposed thereby.

Basic Perfluoride of Cacodyl.

BUNSEN. *Ann. Pharm.* 46, 45.

Concentrated hydrofluoric acid dissolves cacodylic acid abundantly and with great evolution of heat. The solution evaporated in the water-bath, whereby the excess of hydrofluoric acid is driven off, leaves a liquid which solidifies in prisms on cooling. These crystals are pressed between paper, dried in vacuo over oil of vitriol and lime, and kept in platinum vessels.

Long, transparent, colourless prisms, or by quick crystallization, flexible needles. Inodorous.

Calc. according to Bunsen.			Calc. according to Gm.			Bunsen.
12 C	72·0	15·06	8 C	48·0	15·06	15·33
3 As	225·0	47·05	2 As	150·0	47·05	
21 H	21·0	4·39	14 H	14·0	4·39	4·42
6 F	112·2	23·46	4 F	74·8	23·46	23·38
6 O	48·0	10·04	4 O	32·0	10·04	
	478·2	100·00		318·8	100·00	

According to Bunsen, $= 2C^4AsH^6F^3, C^4AsH^6O^3 + 3HO$; according to Gm. $= C^4AsH^7F^4, C^4AsH^7O^4$.

The compound fuses when heated, giving off hydrofluoric acid, and afterwards products having the odour of alkarsin, and finally burns away with a dull grey arsenical flame, leaving a very combustible charcoal. It attacks glass, deliquesces in the air, and dissolves readily in water, forming a liquid which strongly reddens litmus (Bunsen).

Conjugated Compound.

Cyanide of Cacodyl. $C^6NAsH^6 = C^4ArH^3, C^2NH$.

BUNSEN. *Ann. Pharm.* 27, 23.

Preparation. — The danger of poisoning in this process is so great, that it must be performed in the open air; and during the more dangerous manipulations, the air should be inhaled through a long glass tube, the other end of which is far removed from the rising vapour of cyanide of cacodyl. — 1. Alkarsin is distilled with concentrated hydrocyanic acid, and the cyanide of cacodyl freed from admixed alkarsin by crystallization. The purification is imperfect, and in consequence of the ready oxidability of the alkarsin and the fearfully poisonous nature of the cyanide of cacodyl, very dangerous. — 2. Better: alkarsin is added to a concentrated aqueous solution of mercuric cyanide—whereupon mercury is precipitated, and part of the alkarsin passes to a higher state of oxidation—and the mixture distilled. Water then passes over without a trace of alkarsin or hydrocyanic acid, and below it an oily mixture of cyanide of cacodyl and oxidized alkarsin, from which, on cooling, the cyanide of cacodyl crystallizes in large prisms. The water and the liquid portion of the oil are then allowed to run off; the crystals pressed between paper, fused, and freed from water by distilling them to one-half in the apparatus (p. 321) filled with dry carbonic acid. As the quickly crystallizing distillate thus obtained still contains traces of impurities, the tube is broken close to the bulb which serves as a receiver; the contents transferred to the shorter arm of a tube bent at right angles and filled with carbonic acid gas; the open end quickly sealed; the shorter arm heated in water to 50°—60°; the fused mass left to solidify till two-thirds of it have crystallized; the last third, which still remains liquid, drained off into the longer arm; and this melting and partial solidification of the two-thirds, repeated till the portion which runs off no longer exhibits a yellowish colour. The product which then remains in the shorter arm is perfectly pure cyanide of cacodyl.

Properties. Crystallizes on cooling after fusion in large prisms having an adamantine lustre; still more beautifully when sublimed at ordinary temperatures in a glass tube whose upper part is cooled by sprinkling with water; it then forms slightly oblique prisms having their two acute lateral edges slightly truncated, and their ends bevelled with two faces. Cyanide of cacodyl melts at 33°, forming a colourless, ethereal, strongly refracting liquid, which crystallizes again at 32·5°. Boils near 140°, and yields a vapour whose density is 4·63. It is intensely poisonous, more so indeed than any other cacodyl-compound. A few grains of it diffused through the air of a room, are sufficient to excite giddiness, delirium, loss of consciousness, fainting fits, and numbness of the feet: these attacks however are of short duration, and produce no permanent injury, provided the person affected make his escape in time.

			Bunsen.		Vol.	Density.
6 C	36	27·48	28·01	C-vapour	6	2·4960
N	14	10·69	11·05	N-gas	1	0·9706
As	75	57·25	56·43	As-vapour	½	5·1998
6 H	6	4·58	4·61	H-gas	6	0·4158
C^6NAsH^6	131	100·00	100·10		2	9·0822
					1	4·5411

Decompositions. 1. Cyanide of cacodyl when set on fire burns with a red blue flame, emitting a thick fume of arsenious acid. — 2. It reduces the mercury from mercurous (but not from mercuric) nitrate. — 3. With corrosive sublimate, it immediately forms a copious precipitate of the compound of alkarsin and mercuric chloride. — 4. From nitrate of silver it throws down cyanide of silver. Its solution mixed with ferrous salts forms with potash] a precipitate, which, when dissolved in the stronger acids (but not in acetic acid), leaves prussian blue.

Combinations. Cyanide of cacodyl dissolves sparingly in *Water*, very readily in *Alcohol* and *Ether*.

Arsidogen-nucleus. C^4Ar^2O.

Erytharsin. $C^4AsH^6O^3 = C^4Ar^2O,O^2$.

Bunsen. *Ann. Pharm.* 42, 41.

Formation. 1. By passing the vapour of alkarsin or cacodyl through a heated tube. In the case of alkarsin:

$$3C^4AsH^6O = C^4As^2H^6O^3 + C^4H^4 + 2C^2H^4.$$

[in the case of cacodyl, the required oxygen is perhaps supplied by the air of the tube]. — 2. By the imperfect combustion of alkarsin or cacodyl, in which case however the product is always contaminated with an irremovable impurity, as well as with metallic arsenic. — 3. In the preparation of chloride of cacodyl. — 4. Cadet's liquid (p. 315) once distilled under a layer of water has also been observed to deposit erythrarsin.

Preparation. When strong hydrochloric acid is poured upon alkarsin, the chloride of cacodyl which forms, deposits erythrarsin in brick-red flakes, which, after the chloride of cacodyl has been distilled off, remain in the retort united in denser masses, and must be purified by boiling six or eight times with absolute alcohol (which may be done without excluding the air) till the alcohol no longer extracts chlorine, and then dried in the air. By this process, 100 pts. alkarsin yield ½ pt. erythrarsin.

Properties. Dark red, with steel blue iridescence, and yielding a brick-red powder.

			Bunsen.
4 C	24	8·60	8·58
3 As	225	80·65	81·56
6 H	6	2·15	2·08
3 O	24	8·60	7·78
$C^4As^2H^6O^3$	279	100·00	100·00

Decompositions. — 1. Erythrarsin heated in the air burns with a dull grey arsenical flame and without residue. — 2. Exposed to the air in the form of powder, it slowly absorbs oxygen, and in a few weeks becomes covered with a white powder probably consisting of arsenious acid. — 3. It is set on fire by fuming nitric acid, and dissolves readily and without decomposition in the strong non-fuming acid.

Erythrarsin is insoluble in water, potash-ley (which does not decompose it), alcohol, and ether (Bunsen).

Appendix to Cacodyl.

¶ Arsentrimethyl $(C^2H^3)^3As$ and Arsenmethylium $(C^2H^3)^4As$.

A. Cahours & A. Riche. *Compt. rend.* 39, 541.

When iodide of methyl is dropped by small portions at a time into a small flask filled with carbonic acid and containing pulverized arsenide of sodium, a considerable degree of heat is developed; and if the additions of iodide of methyl be repeated till no further rise of temperature is produced, and the mixture be then distilled in a current of carbonic acid, four products are obtained, viz. unaltered iodide of methyl, a white crystalline body, and a heavy liquid composed of two distinct compounds, one of which boils at 120°, the other between 165° and 170°. The former is *Arsentrimethyl;* the latter, *Arsenbimethyl* or *Cacodyl.* The quantity of these liquids obtained is but small, even when the matter operated upon amounts to 100 grammes.

Iodide of Arsenmethylium. — This is the crystallized body just mentioned, which is in fact the chief product of the reaction. It may also be obtained by the action of iodide of methyl upon cacodyl. On mixing these two liquids in a tube, a violent action takes places, and a yellowish white mass of crystals of iodide of arsenmethylium is obtained, impregnated with an oily matter of the same colour, consisting of iodide of cacodyl:

$$2C^2H^3I + 2C^4H^6As = (C^2H^3)^4As,I + C^4H^6As,I.$$

The crystals freed from the oil by draining and pressure between bibulous paper, and then dissolved in iodide of methyl mixed with alcohol, separate from the solution in the form of beautiful colourless tables having a high lustre.

			Cahours & Riche.	
			a.	*b.*
8 C	48	18·39	18·53	18·17
12 H	12	4·60	4·59	4·64
As	75	28·74		
I	126	48·27		
$(C^2H^3)^4AsI$	261	100·00		

a was obtained by the action of iodide of methyl on arsenide of sodium; *b* by that of iodide of methyl on cacodyl.

Iodide of arsenmethylium boiled with recently precipitated oxide of silver, yields a strongly alkaline liquid which, when evaporated in vacuo, yields very deliquescent crystalline laminæ consisting of the *hydrated*

when left to itself, gradually deposits magnificent crystals of iodide of arsenmethylethylium, and likewise yields an oil consisting of iodide of cacodyl.

Bromide. — Bromide of ethyl acts upon cacodyl in a similar manner, but somewhat more slowly.

Chloride. — Hydrochloric ether mixes readily with cacodyl. The mixture enclosed in a sealed tube, does not exhibit any reaction at ordinary temperatures, even after several days; but on heating the tube to 180° or 200°, an oil soon separates and falls to the bottom of the tube, continually increasing in quantity, and containing a number of long colourless needles. If it be then distilled, and only the first portion collected, the remaining portion yields, on cooling, a large quantity of these crystals, which are very deliquescent, and consist of chloride of arsenmethylethylium. The oil consists of chloride of cacodyl.

Mercury compound. — Corrosive sublimate forms with chloride of arsenmethylethylium, a compound which crystallizes in small white needles having the lustre of satin.

Gold compound. — Terchloride of gold forms with chloride of arsenmethylethylium, a compound which crystallizes in small golden-yellow needles.

Platinum compound. — A solution of bichloride of platinum poured into an aqueous solution of chloride of arsenmethylethylium, forms a yellow precipitate, which dissolves in a boiling mixture of equal parts of water and alcohol, and is deposited on cooling in beautiful orange-red needles.

Appendix to the Ethylene-series.

¶ Ferrocyanide of Ethyl. $(C^4H^5)^3FeCy^3 = C^6N^3FeAe^2$.

H. L. Buff. *Ann. Pharm.* 91, 253.

When hydrochloric acid gas is passed into an alcoholic solution of hydroferrocyanic acid, as long as absorption takes place, the liquid being immersed in a frigorific mixture to prevent too great rise of temperature, a solution is obtained, which on cooling, deposits a large quantity of colourless crystals of a compound of ferrocyanide and chloride of ethyl; and on dissolving these crystals in a small quantity of alcohol, and adding ether, ferrocyanide of ethyl is precipitated in white pearly scales, which, after being pressed between paper and then dried very carefully over lime, contain 6 At. water. When left for a considerable time over lime, they part with all their water, and are converted into the anhydrous compound.

	Anhydrous.			Buff.
14 C	84	....	51·22	
10 H	10	....	6·10	
3 N	42	....	25·61	
Fe	28	....	17·07	..... 18·22
$(C^4H^5)^3FeCy^3$	164	....	100·00	

	Crystallized.			Buff.
14 C	84	....	38·53	40·71
16 H	16	....	7·34	6·33
3 N	42	....	19·27	
Fe	28	....	12·84	13·12
6 O	48	....	22·02	
$(C^4H^5)^2FeCy^3 + 6Aq$	218	....	100·00	

The differences between the analytical and calculated results arise from the great proneness of the compound to decomposition.

Chloroferrocyanide of Ethyl. — This is the compound first obtained by passing hydrochloric acid gas into an alcoholic solution of hydroferrocyanic acid. The crystals must be dried between paper, and then placed over lime to free them from adhering water and hydrochloric acid. — When exposed to the air, they quickly decompose and turn blue, from formation of protocyanide of iron. They likewise decompose when placed over lime; great care must therefore be taken to remove them from the lime exactly at the time when they become perfectly dry. When left for a longer time, they give up all their water of crystallization, amounting to 6 Aq.

	Anhydrous.			Buff.
18 C	108·0	....	47·28	
15 H	15·0	....	6·57	
3 N	42·0	....	18·39	
Fe	28·0	....	12·26	12·26
Cl	35·4	....	15·50	
$(C^4H^5)^2FeCy^3 + C^4H^5Cl$	228·4	....	100·00	

	Crystallized.			Buff.
18 C	108·0	....	38·25	37·30
21 H	21·0	....	7·42	7·26
3 N	42·0	....	14·88	
Fe	28·0	....	9·91	9·69
Cl	35·4	....	12·54	12·65
6 O	48·0	....	17·00	
$(C^4H^5)^2FeCy^3 + C^4H^5Cl + 6Aq$	282·4	....	100·00	

This compound mixed with ammonia yields Bunsen's chloroferrocyanide of ammonium, $(NH^4)^2FeCy^3 + NH^4Cl$. (VII, 451) Buff.

Ferridcyanide of Ethyl? Hydrochloric acid gas passed into a mixture of alcohol and ferridcyanide of potassium, is absorbed with great evolution of heat; and if the mixture be well cooled during the passage of the gas, the filtered solution yields, when quite cold, a large quantity of a crystalline, very unstable compound containing chlorine [and probably consisting of ferridcyanide of ethyl united with chloride of ethyl] (Buff).

¶ Thiacetic Acid. $C^4H^4,S^2O^2 = \left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}S^2$.

KEKULÉ. *Proceedings of the Royal Society*, 7, 38; *Ann. Pharm.* 90, 311.

Sulphuretted Acetic Acid, Thiacetsäure.

Formed by the action of tersulphide or pentasulphide of phosphorus* on glacial acetic acid:

$$3C^4H^4O^4 + 2PS^3 = 3C^4H^4S^2O^2 + 2PO^3,$$

and

$$5C^4H^4O^4 + 2PS^5 = 5C^4H^4S^2O^2 + 2PO^5.$$

Also in small quantity, and by secondary action, on distillating acetate of soda with pentachloride of phosphorus.

Colourless liquid soluble in water. Boils at about 93°. Has a peculiar odour, like that of sulphuretted hydrogen and acetic acid together.

				Kekulé.
4 C	24	....	31·58	
4 H	4	....	5·26	
2 S	32	....	42·11	..... 41·3
2 O	16	....	21·05	
$\left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}S^2$	76	....	100·00	

Kekulé, adopting Gerhardt's atomic weights (VII, 17), writes the formula of the acid, $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}S$.

Thiacetic acid is decomposed with explosion by strong nitric acid. Pentachloride of phosphorus acts powerfully on it, forming chlorosulphide of phosphorus, chloride of othyl ($C^4H^3O^2$, Cl), and hydrochloric acid:

$$\left.\begin{matrix}C^4H^3O^2\\H\end{matrix}\right\}S^2 + PCl_5 = PS^2Cl^3 + C^4H^3O^2,Cl + HCl.$$

The acid dissolves potassium, and likewise zinc when heated, with evolution of hydrogen.

Lead-salts. — Thiacetic acid forms with lead a salt which is but sparingly soluble in water, so that the acid precipitates a solution of acetate of lead. The salt may be recrystallized from hot water or alcohol, and then forms needles having a silky lustre, and when recently prepared, perfectly colourless. It decomposes quickly, both in the dry state and in solution, forming sulphide of lead. Strong nitric acid oxidizes it rapidly, forming sulphate of lead and a liquid containing a large quantity of sulphuric acid.

* The sulphides of phosphorus are easily obtained by fusing sulphur with amorphous phosphorus in an atmosphere of carbonic acid. A violent action takes place, but no explosion (Kekulé).

				Kekulé.
4 C	24	....	13·41	
3 H	3	....	1·67	
Pb	104	....	58·10	..... 58·8
2 S	32	....	17·88	
2 O	16	....	8·94	
$C^4H^3O^2$ Pb $\}S^2$	179	....	100·00	

Anhydrous Thiacetic Acid, Sulphide of Othyl, Thiacetate of Othyl. $C^4H^3SO^2 = \begin{matrix} C^4H^3O^2 \\ C^4H^3O^2 \end{matrix}\}S^2$ — Formed by the action of pentasulphide of phosphorus on anhydrous acetic acid:

$$5C^4H^3O^3 + PS^5 = PO^5 + 5C^4H^3SO^2;$$

or:

$$5\begin{matrix} C^4H^3O^2 \\ C^4H^3O^2 \end{matrix}\}O^2 + 2PS^5 = 2PO^5 + 5\begin{matrix} C^4H^3O^2 \\ C^4H^3O^2 \end{matrix}\}S^2.$$

The substances scarcely act upon each other in the cold; but on applying a gentle heat, a brisk reaction takes place; and on distilling the product, anhydrous thiacetic acid is obtained in the form of a colourless liquid, boiling at about 121°, and having an odour like that of the hydrated acid. It sinks in water without decomposing, then gradually dissolves, and is resolved into thiacetic and acetic acid:

$$\begin{matrix} C^4H^3O^2 \\ C^4H^3O^2 \end{matrix}\}S^2 + 2HO = \begin{matrix} C^4H^3O^2 \\ H \end{matrix}\}S^2 + \begin{matrix} C^4H^3O^2 \\ H \end{matrix}\}O^2.$$

The same compound might perhaps be obtained by treating thiacetate of lead with chloride of othyl; at all events, chloride of othyl acts upon this salt, forming chloride of lead (Kekulé).

Thiacetate of Ethyl, or *Thiacetic Ether* $\begin{matrix} C^4H^3O^2 \\ C^4H^5 \end{matrix}\}S^2$.—Produced by the very violent action of pentachloride of phosphorus on acetic ether:

$$5\begin{matrix} C^4H^3O^2 \\ C^4H^5 \end{matrix}\}O^2 + 2PS^5 = 2PO^5 + 5\begin{matrix} C^4H^3O^2 \\ C^4H^5 \end{matrix}\}S^2.$$

Lighter than water, and insoluble in that liquid. — Smells like acetic ether, but with a very strong taint of sulphuretted hydrogen. Boils at 80° C. (Kekulé).

In all these instances, the action of tersulphide and pentasulphide of phosphorus produces sulphuretted organic compounds by substituting sulphur for oxygen. The same compounds may also be formed by replacing the hydrogen in one or two atoms of sulphuretted hydrogen (HS), or the metal in one or two atoms of sulphide of potassium (KS), or in sulphide of hydrogen and potassium (KHS) [or one or two atoms of hydrogen or metal in H^2S, K^2S, &c.] by organic radicals. Mercaptan and the sulphides of the alcohol-radicals have in fact long been obtained in this way (vid. VIII, 340) (Kekulé).

¶ Methyluramine. $C^4N^3H^7$.

DESSAIGNES. *Compt. rend.* 38, 839.

Formation and Preparation. By heating an aqueous solution of creatine or creatinine with mercuric oxide: Carbonic acid is then evolved without a trace of ammonia; the oxide of mercury is partly reduced; and oxalate of methyl-uramine is obtained in crystals:

$$\underbrace{2C^8N^3H^9O^4}_{\text{Creatine.}} + 10O = \underbrace{2C^4N^3H^7,C^4H^2O^8}_{\text{Oxalate of Methyl-uramine.}} + 4CO^2 + 2HO.$$

$$\underbrace{2C^8N^3H^7O^2}_{\text{Creatinine.}} + 10O + 2HO = 2C^4N^3H^7,C^4H^2O^8 + 4CO^2.$$

If the quantity of oxide of mercury be too small, the crystals of oxalate of methyluramine are mixed with crystals of creatine; but when a sufficient quantity of mercuric oxide is used, the oxalate of methyluramine is obtained in large quantity and quite free from creatine. To separate it completely, the solution must be repeatedly treated with alcohol and evaporated.

Methyluramine is obtained in the free state by heating the oxalate with a slight excess of pure milk of lime, and evaporating the filtrate in vacuo.

Properties. White solid body having a crystalline surface, due perhaps to absorption of carbonic acid. Very deliquescent. Its taste is caustic and ammoniacal. Heated on platinum-foil, it volatilizes completely, exhaling a strong odour of burnt creatine:

	Calculation.		
4 C	24	.....	32·88
7 H	7	.....	9·59
3 N	42	.....	57·53
$C^4N^3H^7$	73	.....	100·00

Contains the elements of urea and of methylamine, *minus* 2 At. water (Dessaignes):

$$C^4N^3H^7 + 2HO = C^2N^2H^4O^2 + C^2H^5N.$$

May also be regarded as formed from 2 At. ammonia, by the replacement of 2 At. H by 1 At. cyanogen and 1 At. methyl respectively:

$$C^4N^3H^7 = N^3\begin{cases} C^2N \\ C^2H^3. \\ H^4 \end{cases}$$

This view of its constitution connects it with the cyanic amides (p. 293) (Gerhardt, *Traité de Chimie organique*, 3, 941).

Methyluramine heated with baryta-water is decomposed, giving off ammonia together with an odour of sea-water. It eliminates ammonia from ammoniacal salts at ordinary temperatures. Forms with the chloride of barium and calcium, copious precipitates, which are soluble in a large quantity of water, and in dilute acetic acid. With sulphate of alumina and sesquichloride of iron, it forms precipitates which redissolve in an

excess of the precipitant. It precipitates the salts of lead, copper, and mercury; forms a whitish yellow precipitate with nitrate of silver; and dissolves oxide and chloride of silver.

Combinations. Methyluramine combines with acids, forming crystalline salts, which have a slight alkaline reaction. The *sulphate*, *hydrochlorate*, and *nitrate*, may be easily obtained by decomposing the oxalate with the corresponding lime-salts.

Chloroplatinate of Methyluramine. — A concentrated solution of hydrochlorate of methyluramine mixed with a concentrated solution of bichloride of platinum, yields this salt in the form of splendid orange-coloured rhomboids, which, when redissolved and recrystallized by cooling, often take the form of flat prisms, arranged in parallel groups. The salt when calcined emits an odour of trimethylamine.

	Dried in vacuo.			Dessaignes.
4 C	24·0	8·60		8·77
8 H	8·0	2·87		3·03
3 N	42·0	15·05		14·85
3 Cl	106·2	38·03		38·71
Pt	99·0	35·45		35·19
$C^4N^3H^7,HCl,PtCl^2$	279·2	100·00		100·55

Oxalate. *Preparation*, p. 357. Flattened prisms arranged in parallel groups. Very soluble in water, has a disagreeable taste, and blues reddened litmus slightly. Heated on platinum-foil, it exhales the same odour as creatine.

	Dried at 100°.			Dessaignes. *a.*	*b.*
12 C	72	30·50		30·90	30·98
16 H	16	6·77		6·93	7·27
6 N	84	35·59		35·05	35·43
8 O	64	27·14		27.12	26·32
$2C^4N^3H^7,C^4H^2O^8$	236	100·00		100·00	100·00

	Crystallized.		Dessaignes. *a.*	*b.*
2 $C^4N^3H^7$	146	53·68		
$C^4H^2O^8$	90	33·09		
4 HO	36	13·23	13·25	13·34
$2C^4N^3H^7,C^4H^2O^8+4Aq$	272	100·00		

a was prepared from creatine; *b* from creatinine (Dessaignes).

¶ Tribasic Phosphite of Ethyl. $3C^4H^5O,PO^3$.

R. Railton. *Chem. Soc. Qu. J.* 7, 216; abstr. *Proc. Roy. Soc.* 7, 131.

Formation. By the action of alcohol or ethylate of soda on terchloride of phosphorus:

$$3(HO,C^4H^5O) + PCl^3 = 3HCl + 3C^4H^5O,PO^3 \quad (1)$$

and:

$$3(NaO,C^4H^5O) + PCl^3 = 3NaCl + 3C^4H^5O,PO^3 \quad (2).$$

Preparation. 1. With alcohol. — Absolute alcohol is introduced into a retort which is connected with an apparatus for upward distillation, and surrounded by a freezing mixture; and an equal weight of terchloride of phosphorus added drop by drop. [According to the above equation, 3 At. alcohol are required to 1 At. PCl^3; now 3 At. alcohol = 3 . 46 = 138; and 1 At. PCl^3 = 32 + 3 . 35·4 = 138·2]. The whole is then gently heated for a while, the vapour being allowed to run back into the retort. It is now distilled, and the portion which passes over between 140° and 196°, collected and redistilled, that portion being preserved which boils between 188° and 191°. The quantity of phosphite of ethyl obtained by this process was not large, and there was left in the retort a quantity of phosphorous acid and other products, which on further heating, evolved inflammable phosphuretted hydrogen. — 2. By using ethylate of soda, a much larger product is obtained. The ethylate of soda is prepared by acting upon perfectly absolute alcohol with sodium in a retort, and evaporating to dryness at about 120°; the capacity of the retort should be about three times that of the ethylate of soda produced. The retort is then connected with an apparatus for upward distillation, and a funnel which admits of being closely corked, adapted to the tubulure. (See the Memoir for a figure of the apparatus). For every 69 pts. (3 At.) of sodium used, 138 pts. (1 At.) of terchloride of phosphorus is weighed out, mixed with five times its bulk of pure ether (to moderate the action, which would otherwise be so violent as to set fire to the ethylate of soda), and the mixture introduced into the retort by the funnel, a few drops at a time, the retort during the whole of the process being heated up to the boiling point of ether by a water-bath. After all the terchloride of phosphorus has been added, the heat is continued till the evolved vapour no longer reddens blue litmus-paper. The ether is then distilled off by a water-bath; the retort transferred to an oil-bath; and the oil gradually heated to 200°, at which point it must be steadily maintained till the distillation is terminated. When the operation is carefully conducted, the quantity of phosphite of ethyl obtained is nearly equal to that which is required by equation (2) — The crude product is rectified in a current of hydrogen, as it oxidizes if distilled in air, and the portion which comes over at 188°, is collected and redistilled. — Towards the end of each redistillation, when only a very minute quantity of the substance is left in the retort, a frothing occurs; the thermometer falls; phosphuretted hydrogen is given off; and if the retort be opened at this time, the gas inflames spontaneously, with a violent explosion.

Properties. Neutral, somewhat oily liquid, having a peculiarly offensive odour. Sp. gr. 1·075 at 60° F. Boils at 191° in air, and at 188° in hydrogen. Vapour-density, in one experiment, = 5·800; in another, = 5·877. [These vapour-densities were taken in a globe filled with hydrogen, to prevent the vapour from oxidizing at the high temperature to which it is necessarily exposed. (See *Chem. Soc. Qu. J.* 6, 205)]. — Burns with a bluish flame. Soluble in water, alcohol, and ether.

			Railton (*mean*).			Vol.	Density.
12 C	72	43·11	42·90	C-vapour	12	4·9920	
15 H	15	8·98	8·90	H-gas	15	1·0395	
PO^3	56	33·54	33·24	P-vapour	1	2·1769	
3 O	24	14·37	14·96	O-gas	3	3·3276	
$3C^4H^5O,PO^3$	167	100·00	100·00	Ether-vapour	2	11·6360	
					1	5·7680	

Phosphite of Ethyl and Barium. — *a*. $BaO,2C^4H^5O,PO^3$. — Formed by the action of 1 At. hydrate of baryta on 1 At. tribasic phosphate of ethyl:

$$3C^4H^5O,PO^3 + BaO,HO = BaO,2C^4H^5O,PO^3 + C^4H^6O^2.$$

167 pts. (1 At.) of the phosphite of ethyl are added to 85·6 pts. (1 At.) hydrate of baryta dissolved in hot water, and the whole gently heated for a few minutes. Alcohol is given off; the liquid becomes neutral; and if carefully evaporated in a water-bath, deposits the salt as a confused crystalline mass. — Very deliquescent, extremely soluble in water, soluble also in dilute alcohol, but very sparingly in absolute alcohol. Bears a heat of 108° without decomposing.

	Dried at 108°.			Railton.	
8 C	48·00	23·22	22·65	22·74	
10 H	10·00	4·84	4·95	5·11	
2 O	16·00	7·74	7·98	8·00	
BaO	76·64	37·09	37·32	37·09	
PO^3	56·00	27·11	27·10	27·06	
$BaO,2C^4H^5O,PO^3$	206·64	100·00	100·00	100·00	

The salt with which the analyses were made was recrystallized, dried between blotting paper, then in vacuo over oil of vitriol till it ceased to lose weight, and finally heated to 108° in an oil bath. The deficiency of carbon and excess of hydrogen arise from the extreme deliquescence of the salt.

b. $2BaO,C^4H^5O,PO^3$. — Obtained by the action of 2 At. baryta on 1 At. tribasic phosphite of ethyl:

$$3C^4H^5O,PO^3 + 2(BaO,HO) = 2BaO,C^4H^5O,PO^3 + 2C^4H^6O^2.$$

On gently heating the mixture, alcohol is given off, and the new salt is produced. It does not crystallize.

	Dried at 108°.		Railton.
4 C	24·00	9·75	9·69
5 H	5·00	2·03	2·06
O	8·00	3·25	3·40
2 BaO	153·28	62·23	62·13
PO^3	56·00	22·74	22·72
$2BaO,C^4H^5O,PO^3$	246·28	100·00	100·00

When an excess of baryta is used, a white salt is thrown down on boiling, which appears to be $HO,2BaO,PO^3$ (Railton).

¶ Tribasic Formiate of Ethyl. $3C^4H^5O,C^2HO^3$.

G. Kay. *Chem. Soc. Qu. J.* 7, 224; abstr. *Proc. Roy. Soc.* 7, 135.

Formation. By the action of 3 At. ethylate of soda on 1 At. chloroform:

$$3(C^4H^5O,NaO) + C^2NCl^3 = 3NaCl + 3C^4H^5O,C^2HO^3.$$

Preparation. 1. Sodium is dissolved in absolute alcohol in a tubulated retort, and the excess of alcohol distilled off as much as possible in the oil-bath. Pure chloroform is then added gradually to the dry mass in the proportion of 1 At. to 3 At. of the sodium used. A violent action

takes place at first, rendering it necessary to cool the retort; when this is over, the liquid is distilled off from the chloride of sodium, and subjected to fractional distillation, whereby it is ultimately resolved into three portions, the first of which is small and passes over between 50° and 76°, but chiefly between 50° and 60°; the second, which is the most abundant, and consists of nearly pure alcohol, between 78° and 79°; and the last portion, amounting to one-sixth of the whole liquid, and consisting mainly of the tribasic formic ether, at 145° to 146°. — The lower portion of the first distillate (50° to 76°) had the odour of common ether; part of it treated with sodium, and then mixed with water, became slightly turbid, but did not yield any oily stratum; it contained formic acid and chlorine. — 2. Sodium is dissolved in alcohol to saturation; chloroform added, care being taken to keep the liquid alkaline, and to ensure the decomposition of the chloroform; then more sodium introduced; and the process repeated several times till the liquid becomes bulky. The liquid is then distilled off; again treated with sodium and chloroform as before, and separated from the precipitate; the same operations repeated till about 2 ounces of sodium have been used; and the resulting liquid subjected to fractional distillation: it then divides itself into three portions having the same boiling points as those obtained in (1). — 3. As the preparation of ethylate of soda or potash by the direct action of sodium or potassium on alcohol is somewhat costly, it is better to obtain it by acting upon alcohol with a mixture of potash or soda and lime. Twelve ounces of solid hydrate of potash, and 18 oz. of powdered quicklime are added to rather more than 3 pints of absolute alcohol, and the liquid distilled upwards (cohobated) for five or six hours. Chloroform is then added gradually, in the proportion of 1 At. to 3 At. of the potash used, the cohobation being continued for two or three hours; after which the liquid is distilled off by the heat of an oil-bath, and submitted to a series of fractional distillations. It then divides itself into three portions as before, the highest distillate, which is the tribasic formic ether, and is equal in bulk to about one-sixth of the chloroform used, passing over at 144·5° to 145°. As in the former processes, the lowest distillate had an odour of ether.

Properties. Transparent, colourless liquid, having a peculiar aromatic odour. Sp. gr. 0·8964. When purified by repeated rectification, it boils at 146°. Vapour-density = 5·217. Burns readily with a blue flame and a little smoke. Slightly soluble in water.

			Kay.		Vol.	Density.
14 C	84	56·75	56·51	C-vapour	14	5·8240
16 H	16	10·81	10·40	H-gas	16	1·1088
6 O	48	32·44	33·09	O-gas	3	3·3279
$3C^4H^5O,C^2HO^3$	148	100·00	100·00		2	10·2607
					1	5·1303

May be regarded as chloroform in which the 3 At. chlorine are replaced by 3 At. peroxide of ethyl, $C^4H^5O^2$.

Decompositions. The compound gently heated with very strong oil of vitriol (monohydrated sulphuric acid), then cooled, and slowly added to about its own bulk of ice-cold water, in which a sufficient quantity of baryta is suspended to neutralize the acid employed, yields sulphovinate of baryta, formiate of baryta, and alcohol:

$$3C^4H^5O,C^2HO^3 + 2(HO,SO^3) + 2HO = C^4H^5O,HO,2SO^3 + C^2H^2O^4 + 2C^4H^6O^2.$$

2. Dry hydrochloric acid gas is absorbed in considerable quantity by tribasic formic ether, and appears to convert it into common formic ether C^4H^8O,C^2HO^2. When 1 At. of the gas was passed into 17 grms. of the compound, the gas was wholly absorbed, a considerable amount of heat being evolved and the liquid assuming a brownish colour. When distilled fractionally, it yielded three distillates, the first (about $\frac{1}{2}$) passing over between 20° and 50°; the second (about $\frac{1}{3}$), between 50° and 68°; and the third (one-half) between 68° and 100°. The quantities obtained were however too small to allow of more definite boiling points being obtained. — 2 At. dry hydrochloric acid passed into 29·6 grms. of the liquid were nearly all absorbed, but towards the end of the process a portion passed through. The liquid, which fumed and was strongly acid, was cohobated for some time to expel some of the free hydrochloric acid and then distilled fractionally. About $\frac{1}{2}$ passed over between 50° and 60°; $\frac{1}{3}$ between 60° and 70°; $\frac{1}{8}$ between 70 and 80; and the remainder (about $\frac{1}{4}$) between 80° and 88°. The lowest distillate treated with about an equal bulk of water, floated on the surface, and seemed to be little if at all dissolved. The free acid was neutralized with carbonate of soda, and the liquid pipetted from the water, cohobated for some time over fused chloride of calcium, and then distilled off. The resulting distillate boiled at 55·5°; and had the odour of formic ether. It was found to contain 43·85 p.c. C, and 8·65 H, and its vapour-density was 2·439, whence it was probably formic ether mixed with a small quantity of water (comp. VIII, 483). — The distillate obtained between 60° and 70° yielded a similar product. — 3. Tribasic formic ether treated with *pentachloride of phosphorus*, yields a heavy liquid having the odour of chloroform. — 4. With *potash* it yields a small quantity of formic acid (Kay).

An attempt was made to form the intermediate compounds $C^2H\begin{cases}Cl\\2AeO^2\end{cases}$ = $2AeO,C^2HClO^2$, and $C^2H\begin{cases}Cl^2\\AeO^2\end{cases} = C^4H^8O,C^2HCl^2O$ by adding dry and powdered ethylate of soda very gradually to a large excess of chloroform; but the liquid, when separated from the precipitate and distilled, resolved itself entirely into chloroform, alcohol, and tribasic formic ether (Kay). ¶

COMPOUNDS CONTAINING 6 At. CARBON.

ACRENE SERIES.

A. Primary Series.

Primary Nucleus. Acrene. C^6H^4.

Kryle (Gmelin); *Acrène* (Laurent).

Oxide of Allyl. $C^6H^5O = C^6H^4,HO$.

Wertheim (1844). *Ann. Pharm.* 51, 309; — 55, 297.

Allyloxyd, Oxyde d'Allyle [*Krylather, Lanakryle*].

Sources. Occurs in small quantity in oil of garlic, so that on mixing a very concentrated alcoholic solution of oil of garlic with a very small quantity of nitrate of silver, also in the state of highly concentrated alcoholic solution, a compound of oxide of silver and oxide of allyl is precipitated, without any formation of sulphide of silver.

Formation. 1. By the action of oil of garlic, C^6H^5S, on nitrate of silver, sulphide of silver is precipitated, and a crystalline compound of oxide of allyl and nitrate of silver is formed (p. 364). — 2. By heating oil of mustard with fixed alkalis (vid. *Oil of Mustard*).

Preparation. 1. When the crystalline compound of oxide of allyl with oxide of silver is dissolved in aqueous ammonia, oily drops of oxide of allyl rise to the surface, and may be removed with the pipette and rectified. — 2. Oil of mustard is mixed with soda-lime in one arm of a knee-shaped and sealed glass tube, and heated for some time in the oil-bath to 120°, first for 12 hours in such a direction that the oil of mustard which volatilizes may flow back, and afterwards in such a manner that the empty arm may incline somewhat downwards, and the oxide of allyl which has been formed may distil into it.

Properties. Transparent, colourless oil, having a peculiar odour,

quite different from that of oil of garlic. The preparations (1) and (2) resemble one another exactly.

Calculation, according to Wertheim.

6 C	36	73·47
5 H	5	10·20
O	8	16·33
C^6H^5O	49	100·00

The oil obtained by (2) yields by analysis 4·9 to 5·1 pts. hydrogen to 36 pts. carbon (Wertheim).

Decomposition. Oxide of allyl oxidizes very quickly when exposed to the air.

Nitrate of Silver and Allyl. — A drop of oxide of allyl covered with alcoholic nitrate of silver, immediately becomes filled with crystals of this compound. — When rectified oil of garlic is mixed with an excess of strong alcoholic solution of nitrate of silver, and left in a dark place, nitric acid is set free, and a mixture of sulphide of silver and nitrate of silver and allyl gradually deposited:

$$C^6H^5S + 2(AgO,NO^5) = C^6H^5O,AgO,NO^5 + AgS + NO^5.$$

After 24 hours, the liquid is rapidly heated to the boiling-point, filtered hot from the sulphide of silver, and then left to cool, whereupon it deposits white, highly lustrous prisms united in groups, which, after being washed with alcohol, then with a small quantity of water, and pressed, form a white, shining crystalline powder. The crystals blacken pretty quickly when exposed to light or heated to 100°, but without further perceptible decomposition. When raised to a higher temperature, they burn quickly away with slight detonation, and leave metallic silver. They are quickly decomposed by fuming nitric acid. Hydrochloric acid separates all the silver in the form of chloride, a peculiar odour being at the same time evolved. Sulphuretted hydrogen precipitates sulphide of silver from the solution of the crystals. They dissolve freely in aqueous ammonia, and form a liquid containing argentonitrate of ammonia and having a few drops of oxide of allyl floating on it. — The crystals dissolve readily in water, slowly in cold alcohol and ether, but much more freely in those liquids at higher temperatures.

	Crystallized.		Wertheim.	
			a.	*b.*
6 C	36	16·44	16·22	16·17
5 H	5	2·28	2·26	2·29
Ag	108	49·32	49·21	49·61
N	14	6·39	6·35	
7 O	56	25·57	25·96	
C^6H^5O,AgO,NO^5	219	100·00	100·00	

The crystals *a* were prepared with oil of garlic; *b*, from oxide of allyl prepared by (2).

Acrol. C^6H^4,O^2.

BRANDES. *N. Br. Arch.* 15, 129.
REDTENBACHER. *Ann. Pharm.* 47, 114.

Acrolein, Acryloxydhydrat [*Krylaldid, Nekryle*].

J. A. Buchner (*Mag. Pharm.* 4, 285), by subjecting hog's lard to dry distillation, and partially rectifying the distillate over lime, obtained a pale yellow, very volatile, neutral distillate, which had a pungent odour, dissolved in acids, and abundantly in alcohol. A mouse immersed for one minute in air impregnated with the vapour, and then taken out, died in fifteen minutes. This distillate was undoubtedly rich in acrol. — Brandes (1838) repeatedly rectified with a cooled receiver the empyreumatic oil obtained by dry distillation of cocoa-fat and other glycerides, collecting only the sharp-smelling portion which first passed over; removed the admixed acid and the water by placing the product in contact with carbonate of lime, and afterwards with chloride of calcium; and finally obtained by repeated fractional distillation, a thin, transparent, colourless oil, which evaporated in the air, had a specific gravity of 0·781, and an intolerably sharp odour, like that of concentrated mustard-water. He rightly regarded it as a new compound, *Acrol*, contaminated however with empyreumatic oil. This impure acrol exhibited the following properties. After being kept for some years in a stoppered bottle, it lost nearly all its odour, and then exhibited the character of eupione. It was gradually resinized by oil of vitriol. It was insoluble in water, but when shaken up with that liquid, lost nearly all its sharp odour, the water at the same time becoming slightly acid, but when subsequently distilled with the water, on which it floated, it recovered its odour. When the oil which had been deodorized by agitation with water, was distilled with soda, the first portions which distilled over had a rather sharp odour, but the rest had none; and the residue, when again distilled after supersaturation with phosphoric acid, yielded an oil which had no pungent odour. Aqueous ammonia or potash deprived the impure acrol of its odour, but did not dissolve it. It dissolved in ether and in strong alcohol, but not in spirit of 75 per cent. — Redtenbacher, in 1843, first succeeded in preparing pure acrol, and investigating its properties with accuracy.

Formation. By the dry distillation of glycerine and nearly all glycerides (VII, 227); also by distilling glycerine with anhydrous phosphoric acid, bisulphate of potash, or sulphuric acid.

Preparation. Acrol cannot be obtained in the pure state by the dry distillation of glycerides, because it cannot be completely separated from the empyreumatic oils which are formed at the same time, and some of which have nearly the same boiling-point. Neither is the dry distillation of glycerine itself adapted to the purpose, since the greater part of the glycerine passes over undecomposed, and the residue froths over. — The best mode of preparation is to distil glycerine with an excess of anhydrous phosphoric acid or bisulphate of potash. — When phosphoric acid is used, the distillate consists entirely of acrol, but the viscid residue

is very apt to froth over; when bisulphate of potash is employed, the distillate is contaminated with acrylic acid, sulphurous acid, and other products. The vapours are passed through a condensing tube surrounded with cold water, into a well-cooled tubulated receiver, to the tubulus of which is adapted a long tube, to convey the uncondensed vapours into an empty bladder, or into the chimney, or out of the window, so that they may not hurt the eyes of the operator. — The entire distillate, consisting of a lower watery layer (an aqueous solution of acrol, and perhaps also of acrylic and sulphurous acids) and an upper oily stratum (a mixture of acrol and an oil which smells like acrylic resin) is digested with oxide of lead till the acid reaction disappears; the acrol, together with a small quantity of water, distilled off in the water-bath; the distillate left in contact with perfectly neutral chloride of calcium, and separated therefrom by redistillation on the water-bath. — As acrol oxidizes very rapidly in the air, all these operations, from the digestion with oxide of lead to the final distillation, must be performed in a connected apparatus previously filled with dry carbonic acid gas. To protect the eyes also, the last receiver, which is otherwise closed, must be connected with a chloride of calcium tube, and this connected air-tight with a bladder full of carbonic acid; at the beginning of the operation, the apparatus is filled with the gas by compressing this bladder, and during the distillation, part of the gas again goes into it. Without these precautions, the acrol would acquire an acid reaction, and its vapour mixing with the air would attack the eyes terribly. The quantity of acrol obtained varies according to the heat applied in distilling the glycerine with phosphoric acid or bisulphate of potash, but is always small (Redtenbacher).

Properties. Transparent, colourless oil, which refracts light strongly, and is lighter than water. Boils at about 52°, and yields a vapour whose density is 1·897. The vapour, when diluted with a very large quantity of air, has a somewhat ethereal and not altogether unpleasant odour; but even a few drops of acrol evaporating in a room, are enough to bring a whole company to tears, causing also violent burning and reddening of the eyes, and a feeling of lassitude, which, if the quantity of acrol is somewhat larger, may increase to fainting, but produces no further bad consequences. If, however, the exposure to the vapour be often repeated, every fresh exposure produces inflammation of the eyes, which lasts for several days. Acrol has a burning taste. In the pure state or in aqueous solution, it does not redden litmus paper, so long as no acrylic acid is formed from it by the action of the air (Redtenbacher).

			Redtenbacher.			Vol.		Density.
6 C	36	....	64·29	....	64·58	C-vapour	6	.... 2·4960
4 H	4	....	7·14	....	7·38	H-gas	4	.... 0·2772
2 O	16	....	28·57	....	28·04	O-gas	1	.... 1·1093
C^6H^4,O^2	56	....	100·00	....	100·00	Acrol-vapour	2	.... 3·8825
							1	.... 1·9412

The analysis by Redtenbacher given in the table, yielded the greatest quantity of carbon; in four other analyses, the amount of carbon varied from 61·93 to 63·57. — The radical-theory supposes acrol to contain a hypothetical radical *Acryl* = C^6H^3, which, with 1 O, forms the hypothetical *Oxide of Acryl* = C^6H^3,O; and this with HO forms acrol or

Hydrated Oxide of Acryl = $C^6H^3O + HO$. — Mesitic aldehyde (p. 26) is isomeric with acrol.

Decompositions. 1. Acrol remains but a short time unaltered, even in close vessels, soon becoming turbid and then solidifying in the form of disacryl, partly flocculent, partly compact (or in rare cases, as disacryl-resin). Solidification often takes place in a few minutes after the purification of the acrol, even when it is enclosed in a sealed tube; likewise under water, which then takes up acrylic, formic, and a large quantity of acetic acid. If the sealed tube be opened after several weeks only, the solidified mass contained in it still emits the odour of acrol, and reddens litmus not immediately, but after a short time. According to Redtenbacher's view, the acrol is hereby resolved into disacryl and a hydrocarbon which remains mixed with it, but in presence of air and water, produces the three acids:

$$2C^6H^4O^2 = \underbrace{C^{10}H^7O^4}_{\text{Disacryl.}} + C^2H.$$

[Disacryl is perhaps a compound polymeric with acrol, corresponding to the polymeric compounds of aldehyde (VIII, 281), and its formation is independent of the production of acid which takes place at the same time under water].

2. Acrol passed through a red-hot tube yields carburetted hydrogen gas, water, and charcoal, which is deposited on the sides of the vessel. — 3. It is easily set on fire, and burns with a bright white flame. — 4. When exposed to the air at ordinary temperatures, it is converted, partly as in (1) into disacryl, partly, by rapid absorption of oxygen, into acrylic acid. The aqueous solution likewise quickly takes fire on exposure to the air. A drop of acrol placed upon litmus paper, solidifies in the form of a white powder, round which the paper exhibits a red colour. In some instances, no disacryl is formed but only a red spot. — 5. With chlorine or bromine, acrol forms hydrochloric or hydrobromic acid and a heavy volatile oil, from which it is difficult to expel the last traces of the hydrogen-acid.

6. Acrol dissolves in nitric acid, with copious evolution of nitric oxide, amounting almost to explosion, and forms acrylic acid. — 7. By cold oil of vitriol, it is immediately blackened and carbonized, with evolution of sulphurous acid. — 8. From oxide of silver it reduces the metal, with evolution of heat which rises to the boiling point, and formation of acrylate of silver:

$$C^6H^4O^2 + 3AgO = C^6H^3AgO^4 + 2Ag + HO.$$

With nitrate of silver, acrol forms a white, curdy precipitate, which when left for some time under the liquid, or collected on a filter and washed, is completely reduced to metallic silver, the odour of acrylic and acetic acid being likewise evolved. This precipitate is perhaps a compound of oxide of silver with *acrylous acid*, a substance not otherwise known: that is to say = $AgO,C^6H^3O^2$. [According to the nucleus-theory, this formula is scarcely admissible.] When a few drops of ammonia are added to the mixture of acrol and nitrate of silver, and the liquid boiled, the silver is likewise reduced, but not in the form of a mirror. — Acrol may be distilled without alteration over peroxide of lead. — 9. Aqueous fixed alkalis act strongly upon acrol, converting its sharp odour into an odour like that of cinnamon, and producing two or three different acrylic resins.

Combinations. Acrol dissolves in about 40 pts. of water at 15°, imparting its taste and odour: the solution quickly turns acid on exposure to the air.

When an ethereal solution of acrol is brought in contact with ammoniacal gas or aqueous *Ammonia*, the odour of the acrol gradually disappears, and a white, amorphous, inodorous, and indifferent body separates out.

Ether is the best solvent of acrol (Redtenbacher).

Appendix to Acrol.

Disacryl.

REDTENBACHER. *Ann. Pharm.* 47, 141.

Formation (p. 367).

Preparation. — 1. Acrol is placed under water till it has deposited white, curdy flakes, which must then be washed with water. — 2. The most volatile products of a distilled glyceride are immersed in water, till the water becomes acid and disacryl is formed; the disacryl is then freed from the admixed empyreumatic oils, by washing on a filter with alcohol.

Properties. Fine, loosely coherent, amorphous powder; tasteless, inodorous, and becoming strongly electric by friction.

	Calculation, according to Redtenbacher.		Redtenbacher.
10 C	60	60·61	61·16
7 H	7	7·07	7·43
4 O	32	32·32	31·41
$C^{10}H^7O^4$	99	100·00	100·00

[Perhaps polymeric with acrol, therefore possibly = $C^{12}H^8O^4$.]

Disacryl dissolves slowly in melting hydrate of potash; acids added to the aqueous solution of the resulting mass throw down whitish flakes.

Disacryl is insoluble in water, acids, alkalis, sulphide of carbon, and oils both fixed and volatile (Redtenbacher).

Acryl-Resins.

Acrol treated with an aqueous fixed alkali, is converted into a resinous mass, part of which remains dissolved in the alkali. Instead of pure acrol, the most volatile product obtained by the distillation of a glyceride may be used. Hydrate of lime turns this liquid brown, and becomes surrounded with a brown, dendritic, resinous mass, part of which is soluble in a mixture of ether and alcohol, the rest insoluble.

a. The resin insoluble in a mixture of ether and alcohol, when freed by distillation from the solvent and washed with water and hydrochloric acid, forms a light yellow powder, having an odour of cinnamon.

b. The portion insoluble in ether and alcohol, when mixed and com-

bined with lime, and treated, first with cold, then with hot water, yield an aqueous solution of a compound of resin and lime, from which hydrochloric acid throws down yellow flocks of a resin *b*, *a*. — The portion insoluble in hot water, when purified by hydrochloric acid and water, yields the resin, *b*, *β*.

All these three resins are very difficult to dry on the water-bath; they become strongly electrical by friction (Redtenbacher, *Ann. Pharm.* 47, 146).

		Redtenbacher.	
	a.	*b*, *a*.	*b*, *β*.
C	59·03	59·15	60·04
H	6·69	7·00	7·47
O	34·28	33·85	32·49
	100·00	100·00	100·00

Disacryl-resin.

Once obtained instead of disacryl, from acryl which had been kept for some time, probably because the mass after solidification had been too quickly thrown on the filter and washed.

White powder, fusing at 100°, and solidifying when cold, in the form of a pale yellow, transparent, brittle mass. Separates from the alcoholic solution by evaporation, in shining, brittle, amorphous scales. In the state of alcoholic solution, it reddens litmus.

Insoluble in water, but soluble in aqueous alkalis, from which it is precipitated by acids, with separation of a milky liquid, and separates in coherent masses when heated. — Its alcoholic solution precipitates the salts of lead, copper, and other heavy metals. — It dissolves in ether and in alcohol. The latter solution forms with water a milky liquid, from which the resin separates in the aggregated state on heating the mixture (Redtenbacher, *Ann. Pharm.* 47, 144).

Calculation, according to Redtenbacher.			Redtenbacher.
20 C	120	66·30	66·58
13 H	13	7·18	7·39
6 O	48	26·52	26·03
	181	100·00	100·00

Acrylic Acid. $C^6H^4O^4$.

REDTENBACHER. *Ann. Pharm.* 47, 125.

Acrylsäure, Acide acrylique. — Discovered by Redtenbacher in 1843.

Formation. By the action of air, nitric acid, or oxide of silver, on dry or aqueous acrol (p. 367).

Preparation. a. Of the Silver-salt. A glyceride is subjected to dry distillation; the more volatile products collected in a cooled Woulfe's apparatus; the empyreumatic oils which condense therein, rectified; only the portion which passes over up to 60°, collected; and impure acrol obtained from it by rectification over chloride of calcium. This impure acrol is poured through an S-tube into a flask containing oxide of silver, and

having inserted through its cork another long tube which passes upwards and must be kept cool, so that the acrol-vapours, rising from the liquid, which soon begins to boil, may condense and flow back. When the liquid has stood till the odour of acrol is no longer perceptible, which sometimes takes several days, small quantities of water are repeatedly introduced into the flask, and the liquid repeatedly distilled, till no more empyreumatic oil (colourless and smelling like eupione) passes over. The residue in the flask is then boiled up with a larger quantity of water; the liquid filtered hot from the reduced silver; the crystallization of the acrylate of silver effected by cooling in the dark; and the residue in the flask repeatedly boiled with the mother-liquor of the crystals obtained at each operation, as long as the filtrate continues to yield crystals on cooling. The mother-liquid ultimately remaining, still yields, when exposed to a freezing temperature, a few white, pearly, crystalline scales, but does not deposit any more crystals on evaporation, because it is then decomposed, with reduction of silver and evolution of acrylic and acetic acid. The crops of acrylate of silver obtained by repeated cooling, form cauliflower-like bundles, of the size of nuts, which, if covered with a fine powder of reduced silver, may be easily freed from it by levigation. As they still contain empyreumatic oils, and cannot be purified by recrystallization, because they would be thereby in great part decomposed, with reduction of silver, they must be dissolved in water; the silver precipitated by sulphuretted hydrogen; the filtrate neutralized with carbonate of soda, and evaporated to dryness; the soda-salt distilled with sulphuric acid; the distillate of acrylic acid saturated with oxide of silver at a boiling heat, and filtered boiling; and the filtrate cooled: the pure silver-salt is then obtained in shining needles.

b. Preparation of the Free Acid. — Sulphuretted hydrogen is passed over the pure silver-salt contained in a bulb blown in the middle of tube, and surrounded with ice at first, but afterwards heated so that the acid may distil over. The acid is then freed from sulphuretted hydrogen by rectification: the portion which first passes over contains more water than the last third. If the bulb be not cooled, an evolution of heat takes place sufficient to cause slight explosions, attended with partial decomposition of the acid and formation of water. This decomposition is not wholly prevented, even by surrounding the bulb with ice, whence the acid obtained is not quite anhydrous.

Properties. Transparent, colourless liquid, which does not solidify at 0°. Boils above 100°, apparently with greater facility than acetic acid, and passes over undecomposed. [This does not agree with the boiling point theory, according to which, $C^6H^4O^4$ should have a higher boiling point than $C^4H^4O^4$.] — Has a pleasant sour smell like that of acetic acid, but at the same time rather empyreumatic, like sour roast meat. Tastes purely acid, and in the dilute state, like acetic acid containing a small quantity of some empyreumatic substance.

			Redtenbacher.
6 C	36	50·00	47·57
4 H	4	5·56	6·04
4 O	32	44·44	46·39
$C^6H^4O^4$	72	100·00	100·00

In consequence of the unavoidable admixture of a small quantity of water, the quantity of carbon obtained was too small. — According to the radical-theory, the compound is $C^6H^3,O^3 + HO$ = *Hydrated oxide of acryl.*

Decompositions. 1. Acrylic acid is converted by nitric acid and other powerful oxidizing agents, into acetic acid, formic acid, and the oxidation-products of these two acids:

$$C^6H^4O^4 + 2HO + 2O = C^4H^4O^4 + C^2H^2O^4.$$

Dilute sulphuric and hydrochloric acid do not decompose it. — 2 When treated for some time with aqueous fixed alkalis [in excess], it forms acetates.

Combinations. The acid mixes with *Water* in all proportions.

The *Acrylates* exhibit reactions similar to those of the acetates and formiates. They all dissolve readily in water, excepting the silver-salt which dissolves with difficulty.

Acrylate of Soda. The acid neutralized with carbonate of soda, yields on evaporation, small transparent prisms, which effloresce on exposure to the air, give off 32·5 p.c. water at the temperature of the water-bath, and swell up when more strongly heated. They dissolve readily in water.

	At 100°.			Redtenb.				Redtenb.
NaO	31·2	33·12		32·96	NaO	31·2	22·41	
$C^6H^3O^3$	63·0	66·88			$C^6H^3O^3$	63·0	45·27	
					5 HO	45·0	32·32	32·5
$C^6H^3NaO^4$	94·2	100·00			+5Aq	139·2	100·00	

Acrylate of Baryta. — The saturated solution of carbonate of baryta in the aqueous acid dries up by evaporation to a brittle amorphous gum, which contains 54·36 p.c. baryta, and dissolves readily in water and sparingly in alcohol.

Acrylate of Silver. — The perfectly pure salt (pp. 370, 371) dried over oil of vitriol in vacuo, forms flexible needles having a silky lustre, or a sawdust-like powder consisting of delicate needles and having a slight metallic taste. It blackens slowly when exposed to light, but very quickly when heated to 100°, especially if it be moist. When heated above 100°, it detonates very slightly, giving off a yellow acid vapour, and swells up strongly, forming a network of carbide of silver, which does not give off the last traces of carbon till it has been heated for a long time in the air. The aqueous solution of the salt, when evaporated, gives off vapours of acrylic and acetic acid, and deposits nearly all the silver; hence it cannot be recrystallized without great loss. — The silver-salt still contaminated with empyreumatic oil, which crystallizes out as the solution cools (p. 370), forms cauliflower like masses, composed of delicate four-sided prisms with rounded terminations. — The impure salt obtained by the freezing of the mother-liquid (p. 370), consists of white pearly scales (Redtenbacher).

	Crystallized.		Redtenbacher.			
			a.	*b.*	*c.*	*d.*
AgO	116	64·80	64·63	64·15	62·81	63·34
6 C	36	20·11	20·32	20·31	20·71	20·54
3 H	3	1·68	1·86	2·00	1·95	1·98
3 O	24	13·41	13·19	13·54	14·52	14·14
$C^6H^3AgO^4$	179	100·00	100·00	100·00	100·00	100 00

a is the pure needle-shaped, *b* the pure sawdust-like salt; *c* the impure cauliflower-like; *d* the pure scaly salt.

Conjugated Compound.

Acrylic Ether. $C^{10}H^8O^4 = C^4H^3O, C^6H^5O^3$?

Redtenbacher did not succeed in preparing this compound in the pure state.

1. When concentrated acrylic acid is distilled with a mixture of alcohol and oil of vitriol, the distillate purified by aqueous carbonate of soda, then dried over chloride of calcium and rectified, a liquid is obtained, containing only 49·5 p.c. carbon, and consisting chiefly of formic ether, but exhibiting a faint odour of horse-radish. Perhaps the acrylic acid used contained formic acid.

2. When oil of vitriol and alcohol are distilled with acrylate of soda or baryta, and the distillate purified by water and carbonate of soda, a liquid is obtained, which is not very thin, boils at 63°, and has an agreeable aromatic odour, like that of formic ether and of horse-radish. Chloride of calcium, placed in contact with this liquid, takes up water, and becomes at first translucent and crystalline, but after twelve hours, white and pulverulent. The supernatant liquid, though unaltered in odour, is thinner, and yields by rectification a product containing 55·34 per cent C, 9·38 H, and 35·28 O, and therefore exhibiting the composition of acetic ether. But the somewhat too great amount of carbon, and the still perceptible odour of horse-radish, show that undecomposed acrylic ether still remains behind. Either acetic acid was formed as soon as the sulphuric acid began to act, or the acrylic ether formed at the commencement of the process, was subsequently converted by the chloride of calcium, which perhaps contained free lime, into acetic ether (Redtenbacher, *Ann. Pharm.* 47, 131).

Oil of Garlic. $C^6H^5S = C^6H^4, HS$.

WERTHEIM. *Ann. Pharm.* 51, 289; 55, 297.

Sulphide of Allyl, Knoblauchöl, Schwefelallyl [*Schwefelkrylafer, Lafakryle*].— Cadet (*J. Phys.* 95, 106; abstr. *N. Gehl.* 5, 354) examined the oil obtained by distillation from garlic bulbs, and Fourcroy & Vauquelin the oil obtained from the juice of the bulbs of *Allium Cepa*, whereby they obtained the following results: *Oil of garlic* is yellow, heavier than water, very volatile, of powerful odour, sharp taste, and reddens the skin. It blackens recently precipitated hydrated protoxide of iron, but not oxide of bismuth or other metallic oxides. — *Oil of onions* is colourless, volatile, of sharp taste and odour. Its aqueous solution gives a yellow precipitate with neutral acetate of lead; covers the copper still in which it is distilled, with sulphide of copper; and precipitates baryta-salts after being treated with chlorine. — But the first accurate investigation of oil of garlic was made by Wertheim in 1844.

Sources. In the bulb of *Allium sativum;* in the leaves of *Erysimum Alliaria* (*Alliaria off.*) whereas the roots of that plant contain oil of mustard (Wertheim); also, together with 10 per cent of oil of mustard,

in the herb and seeds of *Thlaspi arvense*, passing over when these matters are bruised with water and distilled. — The leaves of *Erysimum Alliaria* when distilled with water yield oil of garlic; the seeds, oil of mustard (Wertheim). The bruised seed distilled after maceration in water, yields a mixture of 10 per cent oil of garlic, and 90 oil of mustard; but the seed produced in sunny places yields only the latter. The herb and seeds of *Thlaspi arvense* yield a mixture of 90 per cent oil of garlic, and 10 oil of mustard. The herb and seeds of *Iberis amara* likewise yield a mixture of the two oils; and very small quantities of the same mixture are obtained from the seeds of *Capsella Bursa Pastoris*, *Raphanus Raphanistrum*, and *Sisymbrium Nasturtium* (Pless, *Ann. Pharm.* 58, 36).

To obtain the whole of the mixed oils, the several parts of the plants, especially the seeds, must be macerated in water some time before distillation. For, in the seeds of *Thlaspi arvense*, for example, the oils do not exist ready formed. The seeds, in fact, emit no odour when bruised; and if before distillation with water, they are heated to 100°, or treated with alcohol, no oil passes over; and if the seed be exhausted with alcohol, and the filtrate evaporated, there remains a crystalline residue mixed with mucus, which, when triturated with water and with the seed of *Sinapis arvensis*, yields, not oil of garlic, but oil of mustard. To separate the two oils, and distinguish them with accuracy, the mixture may be saturated with ammoniacal gas, and distilled with water: thiosinnamine then separates from the residue, and the distillate neutralized with ammonia and distilled with sulphuric acid, yields an oil having a pure garlic odour, and whose alcoholic solution forms with bichloride of platinum, the yellow platinum-precipitate to be described below: from the quantity of this precipitate, that of the garlic-oil may be calculated. Or the mixture of the two oils, after addition of a small quantity of alcohol, may be immediately precipitated by chloride of platinum, the precipitation being accelerated by agitation; the oil of mustard immediately distilled over with water; and the quantity of oil of garlic determined from that of the platinum-precipitate. If the distillation be not performed immediately, the oil of mustard is decomposed in a few days by the excess of chloride of platinum, and the precipitate somewhat increased (Pless, *Ann. Pharm.* 58, 36).

Formation. By treating oil of mustard with protosulphide of potassium, in the manner described for the preparation of oxide of allyl (compare also *Oil of Mustard.* Decompositions).

Preparation. *a. Of crude Oil of Garlic.* By distilling bruised garlic-bulbs with water in a large still. — The oil passes over with the first portions of water, the product amounting to 3 or 4 oz. from 100 pounds of the bulbs. The milky water which passes over at the same time, contains a large quantity of oil in solution, and serves therefore for cohobation. The crude oil is heavier than water, of dark brownish yellow colour, and has a most intense odour of garlic. It decomposes at 140°; that is to say, somewhat below its boiling-point, which is about 150°, becoming suddenly heated, assuming a darker colour, and giving off intolerably stinking vapours, without yielding a trace of garlic-oil; the residue is a black-brown, glutinous mass (Wertheim).

b. Preparation of the rectified oil. The crude oil is distilled in a salt-bath (in the water-bath the distillation is slower) as long as anything passes over. One-third of the crude oil remains behind as a thick dark-

brown residue. — The rectified oil is lighter than water, and of a pale yellow colour, or after two distillations, colourless, and smells like the crude oil, though less offensive. Does not evolve a trace of ammonia when treated with hydrate of potash. It covers potassium with a liver-coloured film of sulphide of potassium, depositing an organic substance, and giving off a small quantity of a gas which burns with a pale blue flame. With fuming nitric acid, oil of vitriol, hydrochloric acid gas, dilute acids and alkalis, corrosive sublimate, nitrate of silver, bichloride of platinum, and nitrate of palladium, it behaves like pure oil of garlic (sulphide of allyl). Even after being several times rectified and dried with chloride of calcium, it exhibits a variable composition and a certain amount of oxygen, and must therefore contain, besides sulphide of allyl, an oxygen-compound, probably oxide of allyl, the presence of which is indeed indicated by the reaction with potassium (Wertheim).

Three samples exhibited the following percentages of C and H:

C	55·39	59·06	60·57
H	7·70	8·19	8·40

c. Preparation of Pure Oil of Garlic or Sulphide of Allyl. The rectified oil is again rectified several times; dehydrated over chloride of calcium; decanted; a few pieces of potassium introduced into it; and as soon as the evolution of gas thereby produced has ceased, the oil is quickly distilled off from the residue. The rectified oil appears to contain oxide and sulphide of allyl, together with excess of sulphur, these impurities either pre-existing in the crude oil, — as already mentioned respecting oxide of allyl (p. 363), — or being formed from sulphide of allyl by the action of atmospheric oxygen, that portion of the sulphide which takes up the oxygen giving up its sulphur to the rest. If the potassium be not suffered to complete its action before the liquid is distilled, it merely removes the excess of sulphur, but does not decompose the oxide of allyl; and a distillate is obtained, containing from 65·17 to 64·75 per cent C, and 9·22 to 9·15 H (Wertheim).

Properties. Colourless oil, of great refracting power, and heavier than water. May be distilled without decomposition. Smells like the crude oil, but less disagreeably; in short, exactly like the rectified oil.

			Wertheim.
6 C	36	63·16	63·22
5 H	5	8·77	8·86
S	16	28·07	27·23
C^6H^5S	57	100·00	99·31

Decompositions. 1. Sulphide of allyl dissolves with violent action in fuming nitric acid; the solution when diluted with water, deposits yellowish white flakes, and is found to contain oxalic and sulphuric acid; according to Hlasiwetz (*J. pr. Chem.* 51, 355) oil of garlic treated with nitric acid, yields formic and oxalic acid. — 2. With cold oil of vitriol, it forms a purple solution, from which it is separated by water, apparently without alteration. — 3. It absorbs hydrochloric acid gas in abundance; the deep indigo-coloured mixture becomes gradually decolorized on exposure to the air, and immediately if gently heated or diluted with water. — 4. From nitrate of silver, it throws down a large quantity of sulphide of silver, whilst nitrate of silver and allyl remains

of gold, a beautiful yellow precipitate, which resembles the platinum-precipitate, but soon cakes together in resinous masses, and becomes covered with gold films (Wertheim).

Platinum-precipitate. — Oil of garlic forms a yellow precipitate with bichloride of platinum. This precipitate is obtained of a finer yellow colour by the use of alcoholic solutions; when strong alcohol is used, however, its formation is gradual, but becomes instantaneous on addition of water. If the water be added too quickly and in too great quantity, the precipitate is yellowish brown, resinous, and difficult to purify; the addition of water must therefore be stopped as soon as a strong turbidity appears; in that case, if the oil of garlic is not in excess, a copious flocculent precipitate is sure to be obtained resembling chloroplatinate of ammonium. The precipitate is washed on the filter, first with alcohol, then with water, and dried at 100°. — When heated considerably above 100°, the precipitate changes colour, and leaves sulphide of platinum, in so porous a condition that it takes fire at a higher temperature, and continues to glow till it is reduced to pure platinum. Fuming nitric acid decomposes and dissolves the precipitate completely, forming bichloride of platinum and platinic sulphate. When immersed in hydrosulphate of ammonia, it is gradually converted into the kermes-brown compound next to be described. Aqueous potash and sulphuretted hydrogen have no action upon it. — The precipitate is nearly insoluble in water, and dissolves but sparingly in alcohol and ether (Wertheim).

	At 100°.				Wertheim.
24 C	144·0	....	17·77	.....	17·85
20 H	20·0	....	2·47	.....	2·87
4 Pt	396·0	....	48·88	.....	48·53
9 S	144·0	....	17·77	.....	18·29
3 Cl	106·2	....	13·11	.....	13·22
$3(C^6H^5S,PtS^2)+(C^6H^5Cl,PtCl^2)$	810·2	....	100·00	.....	100·76

According to this formula, the compound appears to be formed in the manner represented by the following equation:

$$9C^6H^5S + 9PtCl^2 = C^{24}H^{20}Pt^4S^9Cl^3 + 5(C^6H^5Cl,PtCl^2).$$

The last member of this equation appears in fact to be produced in the precipitation; for when strong alcohol is used, golden-yellow, crystalline scales are sometimes obtained, which, however, immediately disappear on diluting the liquid with water (Wertheim).

Kermes-brown compound. C^6H^5S,PtS^2. — Formed, together with dissolved sal-ammoniac, when the platinum-precipitate just described is left in contact and shaken up with aqueous hydrosulphate of ammonia;

$$C^{24}H^{20}Pt^4S^9Cl^3 + 3NH^4S = 4(C^6H^5S,PtS^2) + 3NH^4Cl.$$

The brown compound heated to 100° emits an alliaceous odour, and gives off 4·88 p.c. ($\frac{1}{6}$ At.) sulphide of allyl. The darker substance containing excess of platinum which remains, continues unaltered till it is heated to 140°, but between 150° and 160°, gives off 5·17 per cent more, therefore in all 9·55 per cent ($\frac{1}{3}$ At.) of sulphide of allyl, leaving a still darker compound of $2C^6H^5S$ with $3PtS^2$. The kermes-brown compound is insoluble in water, alcohol, and ether (Wertheim).

Kermes-brown compound, dried in vacuo.

6 C	36	19·15	19·37
5 H	5	2·66	3·11
Pt	99	52·66	52·09
3 S	48	25·53	
C^6H^5S,PtS^2	188	100·00	

Palladium-precipitate. $2C^6H^5S,3PdS$. — Precipitated on gradually adding purified oil of garlic to aqueous nitrate of palladium, which must be in excess. On mixing the alcoholic solutions of the two bodies, the same precipitate is obtained, but mixed with palladium, which is quickly reduced from the nitrate by the alcohol.

Loose, light kermes-brown precipitate, very much like the platinum-compound just described; after washing and drying, it is tasteless and inodorous. — The precipitate, when heated above 100°, gives off the odour of oil of garlic; when more strongly heated, it burns away with a glimmering light, emitting an odour of sulphurous acid, and leaves metallic palladium. It is rapidly oxidized by fuming nitric acid, with formation of sulphuric acid. It is insoluble in water and alcohol (Wertheim).

	Dried at 100°.		Wertheim.
12 C	72·0	22·37	22·24
10 H	10·0	3·11	3·17
3 Pd	159·9	49·67	49·51
5 S	80·0	24·85	
$2C^6H^5S,3PdS$	321·9	100·90	

The formation of this precipitate probably takes place in the manner represented by the following equation:

$$5C^6H^5S + 3(PdO,NO^5) = 2C^6H^5S,3PdS + 3C^6H^5O + 3NO^5.$$

When an alcoholic solution of oil of garlic is precipitated by excess of alcoholic nitrate of palladium, the liquid above the precipitate is of a deep ruby colour, and does not deposit any metal, even after a considerable lapse of time, probably because the excess of nitrate of palladium is protected from reduction by the alcohol, by entering into combination with the oxide of allyl simultaneously formed (Wertheim).

With protochloride of palladium, sulphide of allyl forms a fire-yellow precipitate, probably a compound of a sulphur-salt with a chlorosalt (Wertheim).

Sulphide of allyl dissolves readily in *Alcohol* and *Ether* (Wertheim).

There appears to be a *Persulphide of Allyl*, which sublimes when oil of mustard is heated with persulphide of potassium, and is distinguished by an extremely intense odour of *Asa fœtida* (Wertheim).

Amidogen-nucleus. C^6AdH^3.

¶ Alkali produced by oxidation of Creatine.

$C^6NH^5 = C^6AdH^3$.

DESSAIGNES. *Compt. rend.* 38, 839.

When nitrous gas is passed into a solution of nitrate of creatine, a large quantity of gas is evolved; and on neutralizing the product with potash, separating the greater part of the nitre by crystallization, and then adding nitrate of silver, crystals are obtained which dissolve in hot water, and after several crystallizations, exhibit the form of long white needles, turning slightly yellow on exposure to light. They consist of a compound of the base C^6H^5N with nitrate of silver.

				Dessaignes.
6 C	36	....	16·00	..... 16·29
5 H	5	....	2·22	..... 2·37
2 N	28	....	12·45	
Ag	108	....	48·00	..... 47·97
6 O	48	....	21·33	
$C^6AdH^3,AgNO^6$	225	....	100·00	

This silver-compound decomposed by excess of hydrochloric acid, yields the *Nitrate* of the base C^6H^5N, in the form of a fibrous mass of small prisms, having a very sour taste.

The *Chloromercurate* crystallizes in long prisms (Dessaignes). ¶

Nitrogen-nucleus C^6N^4.

Mellone. C^6N^4.*

LIEBIG. *Pogg.* 15, 557. — *Ann. Pharm.* 10, 4; also *Pogg.* 34, 573. — *Ann. Pharm.* 30, 149; — 50, 337; 53, 330; — 57, 93; — 58, 227; — 61, 262.

L. GMELIN. *Ann. Pharm.* 15, 252.

VÖLCKEL. *Pogg.* 58, 151; — 61, 375.

GERHARDT. *Compt. mensuels*, 1, 24. — *Compt. rend.* 18, 158; also *J. Chim. méd.* 31, 438; also *J. pr. Chem.* 31, 438. — *Compt. mensuels* 6, 104.

LAURENT & GERHARDT. *Compt. rend.* 21, 679. — *N. Ann. Chim. Phys.* 19, 85; abstr. *Compt. rend.* 22, 453.

HENNEBERG. *Ann. Pharm.* 73, 228; *Pharm. Centr.* 1850, 296, 305; *Chem. Gaz.* 1850, 268; *Compt. mensuels* 6, 98; — *Jahresber.* 1850, 363.

Mellan (Berzelius), *Glaucene* (Völckel). — First obtained by Berzelius, in distilling mercuric sulphocyanide (VIII, 94), and by Wöhler in distilling mercurous sulphocyanide (VIII, 94); but Liebig, in 1829, was the first who recognized and examined it with accuracy.

Formation. By very gentle ignition of pseudosulpho-cyanogen, sulphocyanide of mercury, sulphocyanide of ammonium, chlorocyanamide,

* It would perhaps be more correct to raise the formula of mellone to $C^{12}N^9$ (Gm.).

melamine, ammeline, ammelide, or melam, out of contact of air (Liebig), Also by heating hydropersulphocyanic acid (Völckel); or ammonio-iodide, ammonio-bromide, or ammonio-chloride of cyanogen (VIII, 138, 140, 145) (Bineau).

The equations for these several modes of formation are as follows: 1. If we suppose, with Liebig, that mellone = C^6N^4, then, for the formation from *pseudosulphocyanogen* (according to the earlier supposition that this compound = C^2NS^2), we have:

$$4C^2NS^2 = C^6N^4 + 2CS^2 + 4S.$$

(But, if pseudosulphocyanogen contains H, then, since no products containing hydrogen are evolved in the reaction, the hydrogen must remain with the C^6N^4, and consequently, when the temperature is further raised, the nitrogen thereby evolved will at first be accompanied with hydrocyanic vapour instead of cyanogen gas: Liebig). — With *mercuric sulphocyanide:*

$$4C^2NHgS^2 = C^6N^4 + 2CS^2 + 4HgS;$$

with *sulphocyanide of ammonium:*

$$4C^2N(NH^4)S^2 = C^6N^4 + 2CS^2 + 4HS + 4NH^3;$$

with *hydropersulphocyanic acid:*

$$4C^2NHS^2 = C^6N^4 + 2CS^2 + 4HS + 4S.$$

[At all events, Gerhardt adopted this last equation, so long as he regarded mellone as C^6N^4; but according to Liebig (VIII, 106), hydropersulphocyanic acid does not yield mellone]. — With *chlorocyanamide:*

$$C^6N^5H^4Cl = C^6N^4 + NH^4Cl;$$

[Here we meet with the difficulty that, according to Laurent and Gerhardt, chlorocyanide when heated, gives off not only sal-ammoniac, but likewise hydrochloric acid]. — With *melamine:*

$$C^6N^6H^6 = C^6N^4 + 2NH^3;$$

with *ammeline:*

$$C^6N^5H^5O^2 = C^6N^4 + NH^3 + 2HO;$$

with *ammelide:*

$$C^{12}N^9H^9O^6 = 2C^6N^4 + NH^3 + 6HO.$$

2. If, with Laurent & Gerhardt, we suppose that mellone = $C^{12}N^9H^3$, then, we have with *pseudosulphocyanogen:*

$$3C^6N^3HS^5 = C^{12}N^9H^3 + 6CS^2 + 6S;$$

with *sulphocyanide of ammonium*, the product first obtained at a gentle heat is poliene (melamine):

$$4C^2N^2H^4S^2 = C^6N^6H^6 + 2CS^2 + 4HS + 2NH^3;$$

and this melamine at a stronger heat yields mellone:

$$2C^6N^6H^6 = C^{12}N^9H^3 + 3NH^3;$$

with *ammeline:*

$$2C^6N^5H^5O^2 = C^{12}N^9H^3 + NH^3 + 4HO;$$

with *ammelide*, to which Laurent & Gerhardt assign the formula, $C^9N^4H^4O^4$:

$$6C^9N^4H^4O^4 = C^{12}N^9H^3 + \underbrace{3C^6N^3H^3O^6}_{\text{Cyanuric acid.}} + \underbrace{3C^2NHO^2}_{\text{Cyanic acid.}} + 3NH^3.$$

[Laurent & Gerhardt's view does not however explain the formation of mellone, $C^{12}N^9H^3$, from *sulphocyanide of mercury*, unless that compound can be shown to contain hydrogen. — ¶ According to Gerhardt, *Compt. mensuels*, 6, 107, sulphocyanide of mercury contains water of crystallization, which it does not give off without undergoing complete decomposition, and the mellone which it yields always contains 1·5 per cent of hydrogen, just as well as that prepared from pseudosulphocyanogen. ¶]

Preparation. A. Of *crude Mellone.* — Liebig prepared this compound chiefly by heating dried pseudosulphocyanogen to low redness, or by gently heating a mixture of sulphocyanide of potassium and dry chloride of sodium in a stream of chlorine gas, and dissolving out the chlorides of potassium and sodium from the residue by water. The crude mellone obtained by one or other of these processes was generally used by Liebig in the experiments about to be described, for which indeed it is as well adapted as pure mellone. ¶. According to Henneberg, it is best to heat the dry pseudosulphocyanogen, first in an open porcelain basin, and afterwards in a covered porcelain crucible; because, if it be heated in a retort, the sulphur which is given off flows back again, and causes the mellone to cake together. Too much heat must also be avoided, as the mellone then bakes together in hard lumps. The product thus obtained has a light yellow colour with a tinge of grey; a grey or red-brown product may be regarded as a failure. ¶. — 2. As the complete expulsion of the sulphur from the preceding compounds requires strong ignition, and a large portion of the mellone is thereby decomposed, Laurent and Gerhardt prefer preparing it by heating chlorocyanamide till it ceases to give off hydrochloric acid and sal-ammoniac; or ammelin, as long as it gives off ammonia and water; or ammelide as long as ammonia, cyanic and cyanuric acids are evolved from it. — Völckel prepares his glaucene (mellone) by igniting his poliene (melamine or melam ?) for a considerable time; as however the point at which the evolution of ammonia ceases, is identical with that at which the decomposition of the glaucene begins, a large quantity of the latter is lost. Völckel likewise prepares it by rapidly heating hydropersulphocyanic acid in a platinum crucible to bright redness.

Whichever of the above-mentioned bodies may be heated, the product obtained is not *pure* but *crude* mellone, its composition varying considerably, according to the strength and duration of the ignition. Thus, in mellone obtained from pseudosulphocyanogen, the amount of carbon may vary by 2 to 3 per cent, and cold-potash ley extracts hydromellone from it, leaving a residue of pure mellone. When, however, the mellone is decomposed by ignition, the last remaining portions always yield the right proportion of 1 vol. nitrogen gas to 3 vol. cyanogen, and when burned with oxide of copper, the right proportion of 2 vol. nitrogen to 3 vol. carbonic acid (Liebig). — According to the different materials from which mellone is prepared, and to the strength and duration of the ignition, the residue varies in colour from pale-yellow to brown, and likewise in composition (p. 381). When the material contains sulphur, it is particularly necessary to continue the heat for a long time in order to expel the sulphur completely. But all mellone-residues agree in this, that when raised to a higher temperature, they are completely resolved into nitrogen, cyanogen, and vapour of hydrocyanic acid, the relative quantities of these products varying however with the nature of the mellone-residue (Völckel).

B. *Pure Mellone* is best obtained by heating mercurous mellonide in a retort till the evolved mixture of cyanogen and nitrogen gases is three-fourths absorbed by potash-ley (Liebig).

Properties. Pure mellone is a loose, light yellow, strongly staining,

tasteless, and inodorous powder (Liebig). — The crude mellone obtained from sulphocyanide of potassium, common salt and chlorine, or from pseudosulphocyanogen (1), is of a light yellow colour, loose and finely laminar (Liebig). Light yellow with a tinge of grey; (Henneberg). — The so-called glaucene (mellone) prepared from poliene is yellowish-white (Völckel).

Formulæ and calculations, according to:

Liebig.			Völckel.			Laurent & Gerhardt.		
6 C	36	39·13	4 C	24	35·82	12 C	72	35·82
4 N	66	60·87	3 N	42	62·69	9 N	126	62·69
			H	1	1·49	3 H	3	1·49
C^6N^4	92	100·00	C^4N^3H	67	100·00	$C^{12}N^9H^3$	201	100·00

Laurent & Gerhardt's formula is Völckel's trebled.

Analyses by Laurent and Gerhardt.

	a.	*b.*	*c.*	*d.*
C	35·73	35·8	36·4	36·0
N	62·50	62·4	61·9	62·2
H	1·77	1·8	1·7	1·8
	100·00	100·0	100·0	100·0

Analyses by Völckel.

	e.	*f.*	*g.*	*h.*	*i.*	*k.*	*l.*	*m.*	*n.*
C	31·63	36·01	37·02	32·17	36·52	36·31	35·57	32·49	35·07
N						61·92	62·85		
H	1·42	1·75	1·91	2·03	1·71	1·77	1·58	1·89	2·09
						100·00	100·00		

Liebig based his formula on the combustion of crude mellone obtained from pseudosulphocyanogen, with oxide of copper, which yielded 3 vol. carbonic acid gas to 2 vol. nitrogen, and on the decomposition of mellone by simple ignition, whereby he obtained 1 vol. nitrogen gas to 3 vol. cyanogen. — Laurent & Gerhardt ignited their mellone for some time in a platinum crucible before analyzing it; *a* was prepared from pseudosulphocyanogen; *b* from ammelin; *c* from ammelide, and *d* from chlorocyanamide. — The crude mellone *e*, *f*, *g*, analyzed by Völckel, was obtained by variously long ignition of pseudosulphocyanogen prepared with nitric acid; *h* with sulphocyanide of potassium and chlorine gas; *i* and *k* from hydropersulphocyanic acid; *l* from poliene (*i.e.* from the residue obtained by heating sulphocyanide of ammonium); *m* and *n* from sulphocyanide of mercury.

Decompositions. Mellone heated in a closed vessel is gradually but completely resolved into a mixture of 1 vol. nitrogen gas and 3 vol. cyanogen (Liebig):

$$C^6N^4 = 3C^2N + N.$$

It is resolved hereby into nitrogen, cyanogen, and hydrocyanic acid (Völckel):

$$C^4N^3H = C^2NH + C^2N + N.$$

When mellone obtained from ammelide or chlorocyanamide is ignited in a tube, it disappears completely, giving off vapours which smell of ammonia and hydrocyanic acid, and deposit first a red, then a yellow, and lastly a red-brown sublimate. The sublimate gives off ammonia when

treated with potash, and precipitates nitrate of silver. The gaseous mixture evolved at the same time contains a gas (ammonia) which is absorbed by hydrochloric acid, another (cyanogen) which is absorbed by potash, and a non-absorbable gas (nitrogen) the relative quantities of the three being at the beginning of the experiment = 9 : 51 : 40, and at the end = 10 : 30 : 60. Hence it appears, that the decomposition of mellone by heat is not very simple (Laurent & Gerhardt).

2. Mellone heated in dry chlorine gas forms a white volatile substance having a powerful odour, and attacking the eyes very strongly. — 3. Mellone dissolves gradually in boiling nitric acid, continually giving off a gas which contains very little or no nitric oxide, and is resolved into ammonia and cyanylic acid, which crystallizes in long needles:

$$C^6N^4 + 6HO = C^6N^3H^3O^6 + NH^3.$$

The evolution of gas is due to this circumstance, that part of the mellone is more completely decomposed [perhaps into nitrogen and carbonic acid ?] so that the quantity of cyanylic acid obtained is less than that which is required by calculation. As no oxidation takes place in this reaction, it is certainly remarkable that other acids do not decompose mellone in the same manner (Liebig). — 4. Mellone dissolves in oil of vitriol with evolution of ammonia; water added to the solution throws down a white substance different from mellone.

5. Crude mellone is decomposed by potash-ley, even in the cold, giving up hydromellone to it; but at a boiling heat, it dissolves slowly and completely, with continued evolution of ammonia, and forms a potash salt which crystallizes in long needles and contains a peculiar acid (Liebig).

This *peculiar acid* [which, according to Henneberg, is identical with *cyameluric acid*, the acid obtained by heating mellonide of potassium with potash-ley], may be obtained in the free state by dissolving the purified potash-salt (*vid inf.*) in warm dilute nitric acid, and purifying the needles which separate on cooling, by recrystallization (Liebig). ¶ According to Henneberg, the acid is precipitated from its salts by strong nitric or hydrochloric acid in the form of a white powder, from the hot aqueous solution of which, mixed with a few drops of hydrochloric acid, it separates on cooling, in white crusts, with separate crystals projecting from them. It dissolves in 420 pts. water at 17°, more readily in hot water. The acid produces a strong stain, reddens litmus, and decomposes carbonates when heated with them. The crystals contain 16·85 p.c. (5 At. = 17·47 p.c.) water of crystallization, which is completely expelled at 100° — 120°. ¶

Calculation, according to Liebig.			Calculation, according to Völckel.		
8 C	48	31·58	8 C	48	31·37
5 N	70	46·05	5 N	70	45·75
2 H	2	1·32	3 H	3	1·96
4 O	32	21·05	4 O	32	20·92
	152	100·00		153	100·00

Calculation, according to Henneberg.			Calc. according to Laurent & Gerhardt.		
12 C	72	32·44	12 C	72	32·73
7 N	98	44·14	8 N	112	50·91
4 H	4	1·80	4 H	4	1·82
6 O	48	21·62	4 O	32	14·54
	222	100·00		220	100·00

	Liebig's Analyses.				Henneberg's Analysis.	
	a.	*b.*	*c.*			
C	32·30	32·30	30·76	C	32·00	32·08
N	48·00	48·00	46·20	N		
H	1·57	1·86	2·00	H	1·71	2·00
O	18·13	17·84	21·04	O		
Crystallized acid	100·00	100·00	100·00	Acid dried at 100°—120°.		

The acid *a* was purified by one, *b* by two, and *c* by three crystallizations [from water or from nitric acid ?] (Liebig). According to Liebig, the acid may be regarded as a compound of cyanic acid with a mellonic acid, $C^6N^4H^2O^3$. This view would agree better with Völckel's formula, which however requires more hydrogen than is given by most analyses of the acid and its silver-salt. — Laurent & Gerhardt's formula differs considerably from Liebig's analyses, moreover, according to this formula, the acid should be tribasic (see the silver-salt, &c.), whereas it contains only 4 O. On the other hand, this formula gives a very simple explanation of the formation of the acid, with evolution of ammonia, from mellone, supposing that substance = $C^{12}N^9H^3$:

$$C^{12}N^9H^3 + 4HO = C^{12}N^8H^4O^4 + NH^3.$$

Völckel's formula, supposing as he does that mellone = C^4N^3H, gives the equation:

$$4C^4N^3H + 8HO = 2C^8N^5H^3O^4 + 2NH^3.$$

But if we assume, with Liebig, that mellone = C^6N^4, we shall then have, according to Völckel's formula, the improbable equation:

$$12C^6N^4 + 36HO = 9C^8N^5H^3O^4 + 3NH^3.$$

With Liebig's formula of the acid, it is impossible to form an equation unless we suppose other products to be formed at the same time.

The acid decomposes when recrystallized from nitric acid, with formation of ammonia and probably also of cyanuric acid (Liebig). For this decomposition, Laurent & Gerhardt give the equation:

$$C^{12}N^8H^4O^4 + 8HO = 2C^6N^3H^3O^6 + 2NH^3.$$

¶ The acid boiled with nitric acid, deposits a white crystalline substance which appears to be cyanuric acid. At a moderate red heat, the acid turns yellow and decomposes, giving off vapours which smell of cyanic acid, and forming a white crystalline sublimate probably consisting of cyanuric acid. The yellow residue consists of mellone (Henneberg). For this decomposition, Gerhardt (*Compt. mensuels* 6, 106) gives the equation:

$$3C^{12}N^8H^4O^4 = 2C^6N^3H^3O^6 + 2C^{12}N^9H^3. \P$$

Potash-salt. a. Neutral. — 1. Crystallizes from the solution of mellone in boiling potash, or may be precipitated therefrom by an equal volume of alcohol. Purified by recrystallization. Long delicate needles having a silky lustre and strong alkaline reaction. The salt melts when heated, without blackening, giving off ammonia and leaving pure cyanate of potash. Dissolves very easily in water, but is insoluble in alcohol (Liebig). ¶ 2. The same salt is obtained by boiling 1 pt. of mellonide of potassium, 10 pts. of potash-ley of sp. gr. 1·2, and 20 pts. of water (renewed as it evaporates) till the concentrated mass is no longer curdy,

but solidifies in a mass of needle-shaped crystals. The crystals are washed on a filter stopped with asbestus, first with solution of potash, then with alcohol, and recrystallized from boiling water, a small quantity of alcohol being added to the filtrate. On cooling, the salt crystallizes in colourless prismatic needles, having a glassy lustre and often $\frac{1}{4}$ of an inch long. The salt has an alkaline reaction; its taste is soapy at first, but afterwards bitter and irritating. The air-dried salt placed over sulphuric acid or heated to 120°, gives off from 13·86 to 14·03 p.c. (= 6 At.) water. It melts at a low red-heat, giving off, first ammoniacal and afterwards acid vapours; the crystalline residue treated with sulphuric acid evolves the odour of cyanic acid. Dissolves in 7·4 pts. water at 18°, and in 1 or 2 pts. of boiling water. The solution yields white crystalline precipitates with chloride of barium and sulphate of magnesia; a bulky, yellow, amorphous precipitate with sesquichloride of iron; bluish white, crystallo-granular with cupric salts; and with silver salts, a curdy precipitate not very soluble in nitric acid (Henneberg).

Calc. according to Henneberg.			Calc. according to Gerhardt.			Henneberg.
12 C	72·0	21·39	12 C	72·0	21·52	21·59
7 N	98·0	29·12	8 N	112·0	33·48	
H	1·0	0·29	H	1·0	0·30	0·25
3 O	24·0	7·13	O	8·0	2·39	
3 KO	141·6	42·07	3 KO	141·6	42·31	42·04
$C^{12}N^7HK^3O^6$	336·6	100·00	$C^{12}N^8HK^3O^4$	334·6	100·00 ¶	

b. Acid salt. — Acetic or weak nitric acid added to the concentrated solution of *a*, throws down sparingly soluble crystalline scales (Liebig). ¶ Thin laminæ, iridescent in sunshine (Henneberg).

Calc. according to Henneberg.			Calc. according to Gerhardt.			Henneberg.
12 C	72·0	27·68	12 C	72·0	27·90	27·22
7 N	98·0	37·68	8 N	112·0	43·38	
3 H	3·0	1·15	3 H	3·0	1·16	1·21
5 O	40·0	15·38	3 O	24·0	9·28	
KO	47·2	18·11	KO	47·2	18·28	18·00
$C^{12}N^7H^3KO^6$	260·2	100·00	$C^{12}N^8H^3KO^4$	258·2	100·00	

Baryta-salt. — Obtained by adding chloride of barium in excess to a boiling dilute solution of the neutral potash-salt, and again heating the liquid after precipitation. Microscopic needles, very loosely aggregated. The crystals contain water of crystallization, the greater part of which is given off at 100°. At 120°, the salt still retains 1 At. water which is given off at 150°. [The quantity which is given off between 120° and 250° is 1·72° p.c.; by calculation, 1 At. = 2·07 p.c.] The salt dried at 100° gave 16·82 p.c. C, 0·49 H, and 52·66 BaO; dried at 120° it gave 53·19 p.c. BaO, and at 250°, 54·12 BaO. According to these numbers, the formula of the salt dried at 250° is $C^{12}N^7HBa^3O^6$; and that of the salt dried at 100°—120° is $C^{12}N^7HBa^3O^6 + 2$ Aq (Henneberg).

Silver-salt. — The alkaline potash-salt *a* forms with an acid solution of nitrate of silver, and the acid potash-salt with a neutral solution of nitrate of silver, a white curdy precipitate very sparingly soluble in boiling nitric acid (Liebig). Dried at 100°, it forms a white, scarcely blackened, friable mass, still retaining a certain quantity of water, which it does not give off at 130° (Henneberg).

Anhydrous Salt.

Calculation, according to Liebig.				Calculation, according to Völckel.			
8 C	48	....	13·11	8 C	48	....	13·08
5 N	70	....	19·13	5 N	70	....	19·07
				H	1	....	0·27
2 Ag	216	....	59·02	2 Ag	216	....	58·86
4 O	32	....	8·74	4 O	32	....	8·72
$C^8N^5Ag^2O^4$	366	....	100·00	$C^8N^5HAg^2O^4$	367	....	100·00

Calc. according to Henneberg.				Calc. according to Laurent & Gerhardt.				Liebig.
2 C	72	....	13·26	12 C	72	....	13·31	13·55
7 N	98	....	18·05	8 N	112	....	20·70	
H	1	....	0·18	H	1	....	0·18	0·15
3 Ag	324	....	59·67	3 Ag	324	....	59·89	58·50
6 O	48	....	8·84	4 O	32	....	5·92	
$C N^7HAg^3O^6$	543	....	100·00	$C^{12}N^8HAg^3O^4$	541	....	100·00	

¶. *Hydrated salt, dried at* 100°.

Calculation according to Henneberg.				Calculation according to Gerhardt.*				Henneberg.
12 C	72	....	12·83	12 C	72	....	12·88	13·12
7 N	98	....	17·47	8 N	112	....	20·04	
3 H	3	....	0·53	3 H	3	....	0·53	0·54
3 Ag	324	....	57·76	3 Ag	324	....	57·96	57·86
8 O	64	....	11·41	6 O	48	....	8·59	
$C^{12}N^7HAg^3O^6 + 2Aq$	561	....	100·00	$C^{12}N^8HAg^3O^4 + 2Aq$	559	....	100·00 ¶	

The carbonic acid and nitrogen evolved in the combustion of the silver-salt were by volume as 8 : 5 (Liebig).

According to Völckel (*Ann. Pharm.* 62, 97), the same potash-salt is obtained, together with a small quantity of cyanurate of potash, when, instead of mellone, poliene (*i. e.* the residue obtained by gently heating sulphocyanide of ammonium) is dissolved in boiling potash. The acid separated from the potash-salt by a stronger acid, is white; crystallizes from hot water in shining needles; and in the state of aqueous solution, reddens litmus slightly. — When heated in a glass tube, it emits a white fume, then gives off ammonia, and leaves a yellowish residue, which gradually disappears, with evolution of cyanogen. It dissolves sparingly in cold water and alcohol, but with tolerable facility at a boiling heat. The aqueous solution forms a white precipitate with nitrate of silver. The equation for the formation of this acid from poliene is, according to Völckel:

$$4C^6N^6H^6 + 12HO = 3C^8N^5H^3O^4 + 9NH^3.$$

If the heating of pseudosulphocyanogen, or of hydropersulphocyanic acid be interrupted before the evolution of sulphur is terminated, the residue, which contains poliene and not mellone, dissolves in potash-ley with evolution of ammonia, even at ordinary temperatures, and the brownish yellow solution forms with acetic acid a greyish white gelatinous precipitate, which is not hydromellone, but a mixture of sulphur and ammeline. For, its solution in hot nitric acid, filtered from the sulphur, yields on cooling, colourless needles of nitrate of ammeline, which contain

* Gerhardt (*Compt. mensuels*, 6, 106) gives only the calculation of the anhydrous salt.

19·0 per cent C and 3·2 H, and from which ammonia separates pure ammeline. The formation of ammeline from poliene by means of caustic potash takes place as represented by the equation:

$$C^6N^6H^6 + 2HO = C^6N^5H^5O^2 + NH^3.$$

(Laurent & Gerhardt, *N. Ann. Chim. Phys.* 19, 102).

Mellone is insoluble in water, cold dilute acids and alkalis, alcohol, and ether (Liebig).

Hydromellone or *Hydromellonic Acid.*

Hydromellon, Hydromellonsäure, Mellonwasserstoffsäure, Acide mellonhydrique.

Preparation. 1. Aqueous mellonide of potassium is precipitated with nitrate of lead or sulphate of copper; the precipitate carefully washed by boiling with water; then diffused in hot water and decomposed by sulphuretted hydrogen; and the filtrate evaporated. (Gm.) — If the precipitate has been well boiled with water, the hydromellonic acid is nearly free from potassium (Gm.). — 2. When a hot solution of mellonide of potassium is mixed with hydrochloric or nitric acid, the mixture soon becomes turbid, and deposits hydromellonic acid in white flakes, which if the liquid is very concentrated, thicken it to a solid magma (Liebig).

Properties. As obtained by evaporating the aqueous solution (1), it forms white opaque crusts; as obtained by precipitation (2), it forms a white earthy powder which leaves a streak (Gm.). Inodorous, and tasteless. Its solution in boiling water scarcely reddens litmus (Gm.); reddens it strongly (Liebig).

The *composition* of hydromellone is not yet determined with certainty. Liebig (*Ann. Pharm.* 50, 337) formerly supposed that it was free from potassium, and regarded it as C^6N^4H. He found that hydromellone dried at 100,° yielded by combustion with oxide of copper, only 23·44 pts. water (or rather, according to a more recent correction (*Ann. Pharm.* 57, 103), 8·44 pts.) to 100 pts. carbonic acid, and thence concluded that it contained only 1 H to 6 C. — 100 : 8.44 = 6 . 22 (carbonic acid): 10·14 (water).

More recently (*Ann. Pharm.* 57, 111), Liebig pronounces the hydromellone prepared by (2) to be an acid potash-salt, which, after drying at 100°, gives off nitrogen, cyanogen, and hydrocyanic acid when heated, and leaves 17 p.c. cyanide of potassium, whence it is $=C^{18}N^{12}HK$. [According to this formula, the potassium in hydromellone should amount to somewhat more than 12 per cent, whereas the 17 per cent of potassium contains only a little more than 10 per cent]. — According to the same more recent statements, there exists another acid potash-salt, which is obtained in fine white laminæ, on adding hydrochloric acid to the hot solution of mellonide of potassium, till the precipitate redissolves, and leaving the solution to crystallize by cooling. These laminæ contain 22 per cent of potassium [wherein it is remarkable that when a much larger excess of hydrochloric acid is used, a salt is formed much richer in potassium than that which results from the precipitation in (2)] — Lastly, if we endeavour to abstract all the potassium from hydromellone by continued treatment with acid, the hydromellone is resolved, according to Liebig, into ammonia and new products soluble in water. — [It is

possible that hydromellone may, only under peculiar circumstances, contain so much potassium as Liebig more recently found; in the product obtained by (1), Gmelin found by ignition, only slight traces of potassium compounds; and Liebig also (*Ann. Pharm.* 50, 359) in his earlier experiments obtained only traces of cyanide of potassium, or cyanate of potash].

Laurent & Gerhardt treated mellone with potash-ley; precipitated the solution by an acid; washed the gelatinous precipitate with water for three days; and found in it, after drying at 135°, from 29·5 to 30 per cent C and 2·2 to 2 p.c. H. From these results they regard hydromellone at 135° as $C^{12}N^8H^4O^4,2Ag$, stating however that the matter is not satisfactorily determined, because the hydromellone obtained in the manner just described contained a considerable quantity of potash. [It should also be known whether the mellone was treated with cold or with hot potash; in the former case, the potash would (according to Liebig's experiments) have dissolved merely the hydromellone which is generally contained in crude mellone; but if boiling potash were used, the peculiar acid [cyameluric acid] above described (p. 383) should be produced, and would be sufficiently distinguished from hydromellone by its property of crystallizing in needles, by its decomposibility by nitric acid, and by the different constitution of its silver-salt. — Moreover, in the hydromellone precipitated by an acid from mellonide of potassium, and containing potassium, Laurent & Gerhardt found 3·30 p.c. C. and 1·3 H. This acid, after being digested for 24 hours with hydrochloric acid, then washed, and dried at 180°, exhibited, when more strongly heated, the following phenomena, which show that at this temperature it still retains nearly 16 p.c. HO: First, it gave off 10 p.c. of pure water; then 2 p.c. more, but accompanied by white fumes; then, with stronger indications of decomposition, 4 p.c. more. The residue contained potassium.

Laurent & Gerhardt formerly adopted the formula $C^{12}N^8H^4O^4$ halved, $=C^6N^4H^2O^2$, according to which, hydromellone would be an acid aldide. In either case, its composition would be:

	At 180°.	
6 C	36	32·73
4 N	56	50·91
2 H	2	1·82
2 O	16	14·54
$C^6N^4H^2O^2$	110	100·00

Decompositions. 1. Hydromellone heated in a test-tube, decrepitates slightly; gives off water and a large quantity of hydrocyanate of ammonia which is deposited in the upper part of the tube and soon turns brown; produces in the lower part of the tube a white solid opaque sublimate, which dissolves in potash when boiled with it for some time; and leaves a lemon-yellow residue (probably mellone) which disappears on continued ignition (Gm.). — Hydromellone first gives off hydrocyanic acid and nitrogen, then turns yellow and gives off cyanogen, and finally leaves a trace of cyanide of potassium or cyanate of potash (Liebig). (For Laurent & Gerhardt's account of the behaviour of hydromellone when heated, *vid. sup.*) 2. Hydromellone in the recently precipitated and pasty condition, boiled for three or four hours with hydrochloric or nitric acid, yields a clear solution which contains sal-ammoniac and does not become turbid on cooling (Liebig). But when dissolved in strong nitric acid, and evaporated at a boiling heat, it remains undecomposed.

Combinations. Hydromellone dissolves very sparingly in cold *Water*, somewhat more readily in boiling water, the solution becoming milky as it cools but not yielding much solid deposit.

It dissolves quickly and abundantly in strong nitric acid; somewhat more slowly but in equal quantity in *Oil of Vitriol.* Both solutions become milky on addition of water (Gm.).

It is insoluble in alcohol, in ether, and in oils whether fixed or volatile (Liebig).

Mellonides or *Hydromellonates.*

Mellone heated with iodide, bromide, or sulphocyanide of potassium expels the radical and forms mellonide of potassium (Liebig). — Hydromellone heated with iodide of potassium eliminates hydriodic acid and iodine; it abstracts the base from the salts of many vegetable acids, and therefore dissolves in a warm aqueous solution of acetate of potash as readily as in caustic potash or carbonate of potash, forming mellonide of potassium (Liebig). — From aqueous solutions of the mellonides, sulphuric, hydrochloric and nitric acid quickly throw down hydromellone in thick white flakes; acetic acid produces the same effect, but less quickly and completely (Gm.).

Mellonide of Ammonium. — Obtained by precipitating aqueous mellonide of barium with carbonate of ammonia, and evaporating the filtrate. Resembles mellonide of potassium in appearance. Gives off water of crystallization when heated, then turns yellow and gives off ammonia, and afterwards the decomposition-products of hydromellone. Insoluble in alcohol (Liebig).

Mellonide of Potassium. — Formation. 1. By heating mellone with potassium. Combination takes place attended with evolution of light and heat, and formation of a small quantity of ammonia, the hydrogen of which is perhaps supplied by the rock-oil adhering to the potassium. The resulting transparent, easily fusible compound forms with water a solution which smells like bitter almonds, but contains no cyanogen, and yields a thick flocculent precipitate with acids (Liebig). — Even when mellone prepared from ammelide or chlorocyanamide, and in the recently ignited state, is gently heated with potassium, which has been freed from rock-oil by paring with a knife, ammonia is still abundantly evolved, when the fiery combination takes place. Consequently mellone contains hydrogen, and the equation is not $C^6N^4 + K = C^6N^4K$, but $C^{12}N^9H^3 + 2K = C^{12}N^8K^2 + NH^3$ (Laurent & Gerhardt). [The potassium during its exposure to the air might become coated with hydrate of potash, and this is perhaps the source of the hydrogen]. — 2. By fusing mellone with iodide or bromide of potassium (Liebig). — 3. By fusing potassium with melamine (Liebig):

$$C^6N^6H^6 + K = C^6N^4K + 2NH^3.$$

4. By fusing sulphocyanide of potassium at a red heat with mellone, melam, ferrous sulphocyanide, cuprous sulphocyanide, or terchloride of antimony (Liebig). — Mellone heated with sulphocyanide of potassium forms mellonide of potassium and sets free the sulphocyanogen, which is resolved with effervescence into sulphur, sulphide of carbon, and mellone; and the mel-

lone thus set free combines with the rest of the potassium in the sulphocyanide, again liberating sulphocyanogen (Liebig). [If we assume the correctness of Liebig's formulæ, the reaction must take place according to the following equation;

$$4C^2NKS^2 + 3C^6N^4 = 4C^6N^4K + 2CS^2 + 4S.$$

According to this equation, 4 At. sulphocyanide of potassium require 3 At. mellone to convert them completely into mellonide, therefore (3 . 92) = 276 pts. mellone to (4 . 97·2) = 388·8 pts. sulphocyanide of potassium; or, in round numbers, rather more than 2 pts. mellone to 3 pts. sulphocyanide of potassium]. — Melam, ferrous sulphocyanide ($4C^2NFeS^2 = C^6N^4 + 4FeS + 2CS^2$) and cuprous sulphocyanide (VIII, 90) yield mellon at a red heat, and consequently act like that body. The action of terchloride of antimony has already been given (VIII, 83) (Liebig).

Preparation. 1. When the mixture of 2 pts. ferrocyanide of potassium and 1 pt. sulphur, which serves for the preparation of sulphocyanide of potassium (VIII, 79) is heated somewhat above the point at which a sample dissolved in water ceases to give a blue precipitate with ferric salts; the cooled mass dissolved in water; the remaining portion of the iron precipitated from the filtrate by potash; the filtrate evaporated; and the residue well boiled with water: the filtrate, when left for some time in a cool place, deposits white cauliflower-like masses of mellonide of potassium, which must be collected on a filter, and freed from sulphocyanide of potassium by repeated crystallization from hot water and by pressure. (Gm.). — G. Reuss (*Repert.* 69, 343) heated the mixture to dull redness, till it flowed quietly without giving off bubbles; dissolved it in hot water; precipitated any iron that might still be present in the solution, by potash; evaporated the filtrate; and obtained on cooling, the same cauliflower-like masses. — Laurent & Gerhardt (*N. Ann. Chim. Phys.* 19, 107) heat the mixture far above the point at which it gives a blue precipitate with ferric salts; exhaust the cooled mass with cold water; evaporate the filtrate till it solidifies to a curdy mass on cooling; extract the sulphocyanide of potassium from this mass by [cold?] alcohol; wash the undissolved mellonide of potassium with the same; and purify it by recrystallization from water.

2. Twenty parts of roasted ferrocyanide of potassium are heated with 10 pts. of sulphur (better with 11 to 12, according to Henneberg) in a covered iron vessel, till the mixture, when kept in a state of continued fusion, no longer gives out blue flames, proceeding from the combustion of the sulphide of carbon evolved by the decomposition of the sulphocyanide of iron; 1 pound of finely pounded and recently ignited carbonate of potash is then added, whereupon the mass again becomes perfectly fluid and mobile; the mass left to cool, and dissolved in boiling water; the filtrate evaporated and cooled; and the crystallized mellonide of potassium washed on the filter with alcohol, till the liquid which runs through no longer reddens ferric salts. The addition of carbonate of potash increases the quantity of the product (Liebig). [Why carbonate of potash increases the product, and renders the mass more fluid, is a point deserving further inquiry.] — ¶. According to Henneberg, this process yields a purer product than the first, but is less certain in its results. The addition of carbonate of potash does not increase the product; but if the temperature be raised too high, may lead to the reproduction of

ferrocyanide of potassium, instead of the formation of mellonide. The increase in the product observed by Liebig, was perhaps due to the greater fusibility of the mass induced by the carbonate of potash; if that be the case, it might be better to add sulphocyanide of potassium, as it is more fusible than the carbonate, and does not contain oxygen. ¶].

3. One part of crude mellone (obtained from pseudosulphocyanogen) is gradually added to 3 — 4 parts of perfectly dry sulphocyanide of potassium melted in a small tubulated retort of difficultly fusible glass. Each addition causes brisk effervescence, arising from evolution of sulphur, bisulphide of carbon, and ammoniacal products; and the mass becomes more viscid after each addition; but the viscidity disappears on continuing the heat. After all the mellone has been added, the mass is kept in a state of red-hot fusion as long as any combustible vapours which form sulphurous acid when ignited are given off, and till the evolution of cyanogen gas begins; the mass is then left to cool. It is a good sign when numerous stellate groups of needles form at a temperature considerably above the melting point of the sulphocyanide of potassium; if these are not produced, the heat has been too low, or the quantity of mellone added is not sufficient. The mass when cold is dissolved in boiling water; and the solution left to cool till it solidifies in a white magma consisting of delicate interlaced needles of mellonide of potassium, which must be freed from the remaining sulphocyanide of potassium by washing with alcohol, and completely purified by recrystallization from water. [According to the above calculation (p. 389), the prescribed quantity of mellone is too small]. — ¶. Henneberg uses about the same proportions of mellone and sulphocyanide of potassium (1 pt. of mellone to 3—5 of sulphocyanide; a larger proportion of mellone thickens the mass too much, and causes too much frothing), and proceeds in a similar manner, excepting that he heats the mixture by a spirit-lamp in small retorts containing 15 or 20 grammes each; because, when large quantities are operated upon at once, it is necessary to use a charcoal fire, the heat of which is difficult to regulate. After having cleansed the neck of the retort from the brown products which pass over in distillation, he treats the mass with boiling water; filters; adds a few drops of acetic acid; and concentrates in the water-bath. Sometimes a mucilaginous substance separates at this stage of the operation, and does not redissolve in water (*comp.* p. 391). The resulting crystals of mellonide of potassium are purified by boiling the very dilute solution with acetic acid and animal charcoal, the filtered solution being each time neutralized with a few drops of potash-solution. The use of alcohol impedes the complete decoloration of the product; hence the solutions should be made to crystallize by concentration, and alcohol used only in the last stage of the process, to wash the crystals and purify them completely from acetate and sulphocyanide (Henneberg). ¶. — 4. Melam is prepared by gently heating sulphocyanide of ammonium or a mixture of 1 pt. of sulphocyanide of potassium and 1 pt. of sal-ammoniac; well washed; and added, after thorough drying, to an equal quantity of sulphocyanide of potassium kept in a state of fusion at a moderate red heat in a retort. The mass, when thoroughly liquified, is left to cool, and dissolved in boiling water; the mellonide of potassium precipitated from the solution by alcohol; washed with alcohol to purify it completely from sulphocyanide of potassium; dissolved in water; and decolorized by animal charcoal: the filtrate when evaporated and left to cool, deposits snow-white, crystallized mellonide of potassium (Liebig). — 5. Cuprous sulphocyanide (VIII,

90), is precipitated by adding sulphocyanide of potassium to a mixture of 2 pts. cupric sulphate and 3 pts. ferrous sulphate; washed with dilute sulphuric acid, which makes it quite white, and afterwards with water; dried on a brick; and heated, to drive off all the water, in a porcelain basin over an open fire, till it begins to assume a brownish colour. 9 parts of this product are then added gradually and with agitation to 6 pts. of sulphocyanide of potassium fused in an iron crucible provided with a cover and placed in a fire, the heat of which is gradually raised; the crucible, after all the material has been introduced, is covered and heated till the bottom becomes red-hot, and sulphide of carbon is no longer evolved; and 6 parts of finely pounded and recently ignited carbonate of potash stirred up amongst the thick pasty mass, which then rapidly gives off carbonic acid, becomes thinner, and flows quietly, whereupon it is left to cool. By boiling the mass with water, filtering, evaporating, and cooling, a large quantity of crystallized mellonide of potassium is obtained (Liebig). The addition of carbonate of potash increases the product, which is considerable (Liebig). [The atomic weight of sulphocyanide of potassium is 97; that of cuprous sulphocyanide, 122. If for this process we assume the equation:

$$C^2NKS^2 + 3C^2NCu^2S^2 = C^6N^4K + 3Cu^2S + 2CS^2 + S;$$

according to which, 97 pts. of sulphocyanide of potassium and $3 . 122 = 366$ pts. of cuprous sulphocyanide are required, the mellone formed in the process finds exactly the quantity of potassium which it requires for the formation of mellonide of potassium. But with the prescribed proportion of 97 pts. sulphocyanide of potassium to only 65 pts. cuprous sulphocyanide, the quantity of mellone produced is far from sufficient to saturate the potassium. It remains therefore to be explained why, in this case, the addition of carbonate of potash increases the product, and why carbonic acid is thereupon evolved]. Gerhardt did not succeed in preparing mellonide of potassium by this process. — 6. Eight parts of sulphocyanide of potassium are fused with 5 pts. of terchloride of antimony, till all the sulphide of carbon and sulphur have gone off; the residue dissolved in boiling water, and the mellonide of potassium left to crystallize from the filtrate (Liebig).

In all these modes of preparation, it is advantageous to operate on considerable quantities at once, a pound or two for instance (Liebig). [Henneberg, on the other hand, in preparing mellonide of potassium by method (3), operates with small quantities, p. 391]. The resulting mellonide of potassium, after being well washed with alcohol, is free from sulphocyanide, but often exhibits a yellowish colour, arising from the presence of a sulphuretted potassium-compound, from which acetic acid throws down thick gelatinous flakes. Mellonide of potassium exhibiting this impurity must be dissolved in water, and mixed with acetic acid, as long as any precipitate is formed; the filtrate mixed with carbonate of potash till it exhibits a slight alkaline reaction; then evaporated; and set aside to crystallize, which takes place very slowly. If the resulting crystalline mass should still be coloured, it must be mixed with a few drops of acetic acid, then boiled with animal charcoal, filtered, and cooled (Liebig).

Properties. Mellonide of potassium fused at a red heat, forms a yellow, transparent liquid, and, on cooling, solidifies to an opaque mass of needles united in stellate groups, which, in consequence of strong con-

traction, exhibits cavities filled with needles (Liebig). From the hot aqueous solution it crystallizes by slow cooling in white, silky, hydrated needles united in flocculent tufts, which, when the liquid is somewhat concentrated, thicken to a white magma (Liebig). Bitter and neutral to vegetable colours (Gm). Very bitter (Liebig).

	Fused.			Liebig.	*Crystallized.*			Liebig.
6 C	36·0	....	27·44	..... 26·10	C^6N^4K	131·2	.... 74·46	
4 N	56·0	....	42·68					
K	39·2	....	29·88	..... 28·51	5 Aq	45·0	.... 25·54	..... 25·41
H	....		....	..... 0·19				
C^6N^4K	131·2	....	100·00		+5Aq	176·2	....100·00	

As the hydrogen amounts to only 0·07 to 0·30 per cent, it must be regarded as accidental (Liebig). — Laurent & Gerhardt admit the same formula, but doubled = $C^{12}N^8K^2$. According to these chemists, the compound crystallized from water, contains after drying, $C^{12}N^8K^2H^2O^2$: they found in it 27 p.c. potassium.

The crystals effloresce and lose their lustre when exposed to the air; they give off 4 At. water at 120°, and the last atom with slight intumescence at 180°, also when fused. The residual anhydrous mellonide of potassium heated in a retort above its melting point, gives off cyanogen and nitrogen gases, and leaves cyanide of potassium (Liebig):

$$C^6N^4K = C^2NK + 2C^2N + N.$$

The crystallized salt gives off carbonate and hydrocyanate of ammonia before it fuses (Gm.); but if the salt be previously well dried, the formation of these products is scarcely perceptible (Liebig).

Mellonide of potassium oxidizes rapidly when fused in contact with the air, attacking the platinum crucible and forming cyanate of potash, together with another salt much less soluble in water. With chlorate of potash it detonates and takes fire, forming cyanate of potash and a salt which crystallizes from water in fine pearly needles. With nitre it fuses at first without decomposition, but is gradually and partially converted into cyanate of potash (Liebig). — ¶ Mellonide of potassium boiled with dilute potash-ley, forms cyamelurate of potash (p. 383), together with formiate of potash, ammelide, and ammonia (Henneberg):

$$3C^6N^4K + 11HO + KO = \underbrace{C^{12}N^7HK^3O^6}_{\text{cyamelurate of potash.}} + \underbrace{C^2HKO^4}_{\text{formiate of potash.}} + \underbrace{C^4H^3N^3O^2}_{\text{½ At. ammelide.}} + 2NH^3.$$

The presence of formic acid among the products of decomposition was not however distinctly made out. (Henneberg). ¶. — Chlorine gas passed through the aqueous solution of mellonide of potassium, forms a white gummy precipitate which cannot be completely freed from chlorine by water; it dissolves in ammonia, with evolution of gas, forming a yellow solution. Iodine does not decompose mellonide of potassium dissolved in water, even at a boiling heat, but evaporates (Liebig). — Mellonide of potassium dissolves sparingly in cold, abundantly in hot, water. Sulphuric, hydrochloric, or nitric acid added to the solution, throws down hydromellone in thick white flakes (Gm.). Acetic acid produces no precipitate, provided the mellonide of potassium be pure (Liebig). — Mellonide of potassium is nearly insoluble in alcohol, even at a boiling heat; hence the aqueous solution is immediately clouded by alcohol, the mellonide of potassium then crystallizing out.

Mellonide of Sodium. — Obtained by decomposing mellonide of barium with carbonate of soda in the humid way. White hydrated, silky needles, tolerably soluble in water, insoluble in alcohol (Liebig).

Mellonide of Barium. — Aqueous mellonide of potassium forms thick white flakes with chloride of barium (Gm.). They crystallize from the boiling aqueous solution in short transparent needles, containing 6 At. water, 5 At. of which (20·87 p.c.) go off at 130, and requiring a large quantity of boiling water to dissolve them (Liebig).

Mellonide of Strontium. — Obtained like the barium-compound. Dissolves much more readily in water, its boiling saturated solution solidifies in a magma of slender needles (Liebig).

Mellonide of Calcium. — Prepared in a similar manner. Still more soluble in hot water, and separates from the solution in crystals which contain 4 At. water and give up 3 At. (18·05 p.c.) at 120° (Liebig).

Mellonide of Magnesium. — The aqueous mixture of mellonide of potassium and sulphate of magnesia deposits the salt after a while, in white interlaced needles easily soluble in water (Liebig).

The compounds of mellone with barium, strontium, calcium and magnesium dissolve more readily in pure water than in water which contains a baryta, strontia, lime, or magnesia salt in solution (Liebig).

Aqueous mellonide of potassium percipitates *alumina* and *titanium* salts, white; *chromic salts*, bluish white; *bismuth*, *zinc*, *cadmium* and *lead* salts, white; *ferric* salts light brown; *cobalt* salts, pale rose-red; *nickel* salts, bluish white; *cuprous* salts, lemon-yellow; *cupric* salts, siskin-green; *mercurous*, *mercuric*, and *silver* salts, white; *chloride of gold*, yellowish white; and *bichloride of platinum*, brownish yellow (Gm.). It precipitates *chromic* salts, green; *manganous* salts and *tartar-emetic*, white; *ferrous* salts, white with a greenish tinge; *ferric* salts, deep yellow; *cobalt* salts, peach-blosom colour; and *dichloride of copper*, bright yellow (Liebig).

Mellonide of Lead. — Aqueous nitrate of lead is precipitated by mellonide of potassium, and the white pulverulent precipitate freed from adhering potash salt by boiling with water. In drying it cakes together into heavy white masses. The air-dried salt gives off 11·09 p.c. (3 At.) water at 100°, and 14·13 p.c. (4 At.) altogether at 120°. When more strongly heated in contact with the air, it gives off water, ammonia and hydrocyanic acid; yields a white pulverulent sublimate; and leaves a yellow residue, which afterwards becomes red-brown, semi-fused, and interspersed with granules of lead. The lead-salt heated with oil of vitriol, boils up, the intumescence continuing after it is removed from the fire; gives off a large quantity of acid vapours; and produces a large quantity of sulphate of ammonia (Gm.).

	Dried in the air at 20°.				Gm.
6 C	36	....	14·94	.....	15·06
4 N	56	....	23·24	.....	23·15
Pb	104	....	43·15	.....	42·68
5 H	5	....	2·07	.....	2·03
5 O	40	....	16·60	.....	17·08
$C^6N^4Pb + 5HO$	241	....	100·00	.....	100·00

Mellonide of Copper. — Mellonide of potassium forms with cupric sulphate, a beautiful parrot-green precipitate. This compound is but sparingly soluble in boiling water, and when dried at 45°, contains 23·94 per cent (5 At.) water, 4 At. of which it gives off at 120°, turning black at the same time (Liebig). [According to calculation, 5 At. water = 26·8 p.c.]

Mercurous Mellonide. — Mellonide of potassium forms with mercurous nitrate, thick, heavy flakes which turn grey on drying, and when heated give off mercury, probably with formation of mercuric mellonide. The precipitate burnt with oxide of copper, gives off a large quantity of water, probably because it likewise contains hydromellone, precipitated from the mercurial solution by the free acid (Liebig).

Mercuric Mellonide. — Mellonide of potassium forms with corrosive sublimate, in the cold, a thick, gelatinous precipitate; but on the slightest application of heat, the liquid becomes milky, and the precipitate is converted into a fine white powder. The precipitate obtained by either of these methods contains potassium. But if the two solutions be mixed boiling, the mixture becomes turbid on cooling, and yields a precipitate free from potassium, the quantity of mercury in which is diminished by washing. This precipitate, when ignited, first gives off nitrogen gas mixed with cyanogen gas and vapour of hydrocyanic acid, and lastly, a mixture of 1 vol. nitrogen gas to 3 vol. cyanogen (Liebig).

Mellonide of Silver. — Mellonide of potassium forms with solution of nitrate of silver, a white gelatinous precipitate which is anhydrous at 120° (Liebig). The precipitate, even after washing with boiling water, still contains potassium (Laurent & Gerhardt).

				Liebig, at 120°.	Laurent & Gerhardt, at 140°.
6 C	36	....	18		
4 N	56	....	28		
Ag	108	....	54	..... 53·030	..... 52·20
H		....		..... 0·016	..... 0·43
C^6N^4Ag	200	....	100		

Appendix to Mellone.

By heating sulphocyanide of ammonium to various temperatures and for various lengths of time in vacuo, Völckel (*Pogg.* 61, 356), obtained the following compounds, the separate identity of which however remains to be established:

Sulphide of Alphene	=	$C^{10}N^{10}H^{10}S^2$.
Sulphide of Phalene	=	$C^{12}N^{12}H^{12}S^2$.
Sulphide of Phelene	=	$C^{14}N^{14}H^{14}S^2$.
Sulphide of Argene	=	$C^{16}N^{16}H^{16}S^2$.

In a similar manner, Völckel (*Pogg.* 61, 151), obtained from hydropersulphocyanic acid:

Sulphide of Xanthene	=	$C^6N^4H^4S^4$ (the same therefore as hydromellone).
Sulphide of Leucene	=	$C^6N^3H^3S^2$.
Sulphide of Melene	=	$C^7N^4H^4S^6$.
Sulphide of Phalene	=	$C^8N^6H^5S^4$.
Sulphide of Xuthene	=	$C^{10}N^9H^7S^4$.

PROPYLENE SERIES.

A. Primary Series.

¶ *Primary Nucleus. Propylene.* C^6H^6.

Reynolds. *Ann. Pharm.* 71, 119; *Jahresber.* 1849, 426;—further and more fully: *Chem. Soc. Qu. J.* 3, 111; *Ann. Pharm.* 77, 114; *Jahresber.* 1850, 494.

Hofmann. *Chem. Soc. Qu. J.* 3, 121.

Cahours. *Compt. rend.* 31, 291; *J. pr. Chem.* 51, 249; *Pharm. Centr.* 1850, 681; *Jahresber.* 1850, 496.

Berthelot and De Luca. *Compt. rend.* 39, 745.

Tritylene, Metacetene, [*Sixe*].

Formation. — 1. In the decomposition of amylic alcohol by heat. When vapour of amylic alcohol is passed through a long glass-tube kept at a red heat, a liquid (probably the unaltered alcohol) is obtained, together with a gas. If the heat be too low, very little gas is evolved; if it be too high, the product consists almost wholly of marsh gas; but when the temperature is properly regulated, a gas is obtained, which burns with a bright flame and consists about one-half of propylene, the other half being chiefly marsh-gas (Reynolds). — 2. In the decomposition of pelargonic, ethalic, or homologous acids by heat (Cahours). — 3. In the decomposition of valerianic acid by heat. When vapour of valerianic acid is passed through a red-hot tube, a number of liquid products are obtained, varying in quantity according to the heat applied, and a large quantity of gas consisting of carbonic acid, carbonic oxide, hydrocarbons of the general formula C^nH^m, and in some cases perhaps also marsh gas. By treating the gaseous mixture with bromine, the hydrocarbons are absorbed, and the resulting liquid subjected to fractional distillation, yields between 143° and 145°, a liquid mainly consisting of $C^6H^6Br^2$ (A. W. Hofmann). — 3. By the action of iodide of phosphorus on glycerine. When equal parts of crystallized iodide of phosphorus, PI^3, and syrupy glycerine are heated together in a retort, an energetic reaction soon takes place; gaseous propylene is evolved; water and iodopropylene, C^6H^5I, distil over; and a residue is left, consisting of undecomposed glycerine, free iodine, a small quantity of an iodurетted organic compound; some oxygen-acids of phosphorus; and a trace of red phosphorus:

$$2C^6H^8O^6 + PI^3 = C^6H^5I + 4HO + I + C^6H^7O^5PO^3.$$

1 At. iodide of phosphorus with variable quantities of glycerine yields

1 At. C^6H^5I and 4 At. water. To obtain 1 At. free propylene it is necessary to use from 9 to 18 At. iodide of phosphorus. The production of free propylene appears therefore to be of secondary importance compared with that of the iodopropylene (Berthelot & De Luca). — 4. In the decomposition of iodopropylene by zinc and dilute sulphuric acid, or by mercury and hydrochloric or dilute sulphuric acid, the iodine being then replaced by hydrogen:

$$C^6H^5I + 2Zn + HO = C^6H^6 + ZnI + ZnO;$$

and

$$C^6H^5I + 4Hg + HCl = C^6H^6 + Hg^2Cl + Hg^2I.$$

When iodopropylene is mixed with zinc and dilute sulphuric acid, and the mixture gently heated, a gas is evolved containing one-fourth of propylene. If a small quantity of iodopropylene, water, and sulphuric acid, or better, concentrated hydrochloric acid, be introduced into a glass tube standing over mercury, the mercury is attacked and gas is evolved, the action continuing till the iodopropylene is completely decomposed. In this manner $\frac{3}{4}$ of the iodurettted compound may be transformed into propylene (Berthelot & De Luca). 5. The gaseous hydrocarbon evolved, together with hydrogen; by the action of potassium on butyronile [cyanide of propyl], is perhaps propylene (Gm.).

Preparation. 1. By the action of iodide of phosphorus on glycerine (*vid. sup.*). The gas evolved is pure propylene. — 2. By decomposing iodopropylene with mercury and hydrochloric acid 30 grammes of iodopropylene (for the preparation of which see p. 428) are introduced into a small flask together with 150 grammes of mercury and 50 or 60 grammes of fuming hydrochloric acid, and the mixture gently heated: decomposition soon takes place, and about 3 litres of propylene are obtained (Berthelot & De Luca). — 3. By decomposing iodide of propylene, $C^6H^6I^2$, with potash and alcohol (Berthelot & De Luca).

Properties. Colourless gas, which burns with a bright flame.

Calculation.					Vol.		Density.
6 C	36	....	85·71	C-vapour	6	.....	2·4960
6 H	6	....	14·29	H-gas	6	.....	0·4158
C^6H^6	42	....	100·00	Propylene-gas ...	2	.....	2·9118
					1	.....	1·4559

Decomposition. 10 vol. propylene exploded with oxygen absorb 45 2 vol. O and yield 30·4 vol. CO^2. — 10 vol. propylene contain 30 vol. carbon-vapour and 30 vol. H-gas. The 30 vol. C-vapour absorb 30 vol. O and form 30 vol. CO^2; the 30 vol. H. consume 15 vol. O and form water: hence by calculation, 10 vol. propylene should absorb 45 vol. O and form 30 vol. carbonic acid, which agrees very closely with the experimental result (Berthelot & De Luca).

Combinations. 1. Propylene is absorbed by fuming *sulphuric acid* and by ordinary concentrated oil of vitriol (Berthelot and De Luca). — 2. It is quickly absorbed by iodine, bromine, and chlorine, forming compounds corresponding to Dutch liquid (Berthelot & De Luca, Reynolds, Cahours, Hofmann) — 3. *Protochloride of copper* dissolves $1\frac{1}{2}$ times its volume of propylene. — 4. Glacial *acetic acid* dissolves 5 times its volume (Berthelot & De Luca).

¶ Iodide of Propylene. $C^6H^6I^2$.

When a small quantity of iodine is introduced into a bottle containing propylene and the mixture exposed to the sun for an hour, iodide of propylene is obtained in the form of a very heavy liquid, which may be purified by agitating it for a while with potash. — When recently prepared, it is colourless and has an ethereal odour; but by the action of air and light, it rapidly becomes coloured, and then gives off a vapour which exerts an extremely irritating action on the eyes. Sp. gr. 2·490 at 18·5. Remains liquid at −10°. Decomposed by heat. When heated with potash and alcohol, it is decomposed, with copious evolution of propylene (Berthelot & De Luca).

¶ Bromide of Propylene. $C^6H^6Br^2$.

When the gaseous mixture obtained by the decomposition of amylic alcohol at a red heat, is shaken up with small quantities of bromine, till the bromine no longer loses its colour, a heavy oily liquid is obtained which may be purified by washing with water, drying over chloride of calcium, and repeated rectification over quick-lime. The liquid began to boil at 136°; but the boiling point soon rose to 143°, where it remained stationary for some time and then slowly rose to 160°, the residual brown liquid decomposing and giving off hydrobromic acid. By repeatedly rectifying the distillate, the compound was at length obtained in a definite state. When the gas is passed into excess of bromine, a large quantity of substitution-products is formed (Reynolds).

Colourless oil of sp. gr. 1·7 (Reynolds); 1·974 (Cahours). Does not solidify at −20° (Reynolds). Boiling point 143° (Reynolds); 145° (Cahours); between 143° and 145° (Hofmann). Vapour-density 7·3 (Reynolds). Odour slightly alliaceous (Reynolds).

			Reynolds.	Hofmann.		Vol.	Density.
6 C	36	17·82	18·00	18·84	C-vapour	6	2·4960
6 H	6	2·97	3·04	3·19	H-gas	6	0·4158
2 Br	160	79·21	78·83	80·00	Br-vapour	2	11·0930
$C^6H^6Br^2$	202	100·00	99·87	102·03	Vap. of $C^6H^6Br^2$	2	14·0048
						1	7·0024

The compound may also be regarded as *Bromide of Propyl and Hydrogen* = C^6H^5Br,HBr. — Hofmann's product was obtained by the decomposition of valerianic acid (p. 395), and was not sufficient in quantity for complete purification.

Decompositions. 1. Bromide of propylene is decomposed by strong sulphuric acid. — 2. Alcoholic potash acts strongly upon it, yielding a deposit of bromide of potassium, and a distillate from which water separates a heavy, colourless, very mobile and volatile liquid, having an odour like that of decayed fish. This liquid, when dried over chloride of calcium and rectified over quick-lime, does not exhibit a constant boiling point; the portion which passes over between 45° and 56°, contains 29·1 p.c. C and 4·0 H, corresponding nearly to C^6H^5Br; that which distils over between 56° and 60° contains 29·3 C and 4·2 H; and that which distils between 60° and 70°, contains 30·9 C and 4·6 H (Reynolds). — 3. By acting on

bromide of propylene with bromine and distilling the several products with alcoholic potash, Cahours obtained the following compounds:

	Boiling point.	Sp. gr.	Yields by distillation with alcoholic potash.	Boil. point.	Sp. gr.
$C^6H^6Br^2$	145°	1·974	C^6H^5Br	62°	1·472
$C^6H^5Br^3$	192	2·336	$C^6H^4Br^2$	120	1·950
$C^6H^4Br^4$	226	2·469	$C^6H^3Br^3$		
$C^6H^3Br^5$	255	2·601			

¶ Chloride of Propylene. $C^6H^6Cl^2$.

Obtained by the action of chlorine on the crude gas evolved in the decomposition of amylic alcohol (Reynolds, p. 325), or of various fatty acids (Cahours, p. 395). Boiling point 100° to 103° (Reynolds); 104° (Cahours); sp. gr. 1·151 (Cahours).

		Reynolds.		
6 C	36·0	31·92		
6 H	6·0	5·32		
2 Cl	70·8	62·76	62·64	62·55
$C^6H^6Cl^2$	112·8	100·00		

= C^6H^5Cl,HCl. — The sample analysed was dried over chloride of calcium, and rectified several times over quick-lime (Reynolds).

Chloride of propylene treated with alcoholic potash yields products similar to those obtained from the bromide (Reynolds). Cahours, by treating it continuously with chlorine, and distilling the successive products with alcoholic potash, obtained the following compounds:

	Boiling point.	Sp. gr.	Yields by distillation.
$C^6H^6Cl^2$	104°	1·154	C^6H^5Cl
$C^6H^5Cl^3$	170	1·347	$C^6H^4Cl^2$
$C^6H^4Cl^4$	195 to 200°	1·348	C^6H^3Cl
$C^6H^3Cl^5$	220 to 225	?	$C^6H^2Cl^4$
$C^6H^2Cl^6$	240 to 245	1·626	$C^6H\,Cl^5$
$C^6H\,Cl^7$	260	1·731	C^6Cl^6.
C^6Cl^8	280	1·860	

These compounds are homologous with those which are obtained by similar means from Dutch liquid $C^4H^4Cl^2$ (VIII, 380).

¶ Propylic Alcohol. $C^6H^8O^2 = C^6H^6,H^2O^2 = \frac{C^6H^7}{H}O^2$.

Chancel. *Compt. rend.* 37, 410; *Instit.* 1853, 310; *Arch. ph. nat.* 24, 385; *J. pr. Chem.* 60, 205; *Pharm. Centr.* 1853, 824; *Chem. Soc. Qu. J.* 6, 287; *Ann. Pharm.* 87, 127; *Jahresber.* 1853, 127.

*Propionic, Metacetic or Metacetonic Alcohol, Hydrate of Propyl, Hydrated oxide of Propyl; Hydrate of Trityl, Tritylic Alcohol.**

Found in the fusel-oil of brandy prepared from wine-lees (*esprits de marcs*), in which Balard had previously found amylic alcohol. When

* The word *trityl* (from the Greek τριτος) is applied by Gerhardt to the radical C^6H^7, to denote that it occupies the *third* place in the series whose first and second terms are methyl and ethyl respectively. A similar nomenclature is also applied to the other homologous radicals: *e.g. tetryl* = C^8H^9; *pentyl* = $C^{10}H^{11}$; *hexyl* = $C^{12}H^{13}$; *heptyl* = $C^{14}H^{15}$; *octyl* = $C^{16}H^{17}$, &c.

this fusel-oil is distilled, the propylic alcohol passes over in the first portions of the distillate. It is purified by several distillations and by a method which Chancel has not yet published, and dehydrated by agitating it with carbonate of potash, then leaving it in contact with caustic potash, and distilling. Its formation from grape-sugar, together with vinic or amylic alcohol, may be represented by the following equations:

$$2C^{12}H^{12}O^{12} = 2C^6H^8O^2 + C^4H^6O^2 + 8CO^2 + 2HO = C^6H^8O^2 + C^{10}H^{12}O^2 + 8CO^2 + 4HO.$$

The last equation seems to show that the formation of amylic alcohol is necessarily accompanied by that of propylic alcohol.

Properties. Colourless liquid, lighter than water, and having a strong fruity odour. Boils at 96°. Vapour-density = 2·02.

Calculation.					Vol.		Density.
6 C	36	....	60·00	C-vapour	6	....	2·4960
8 H	8	....	13·33	H-gas	8	....	0·5544
2 O	16	....	26·67	O-gas	1	....	1·1093
$C^6H^8O^2$	60	....	100·00	Alcohol-vapour	2	....	4·1597
					1	....	2·0798

Propylic alcohol dissolves in water very abundantly, but not in all proportions, rising to the top in the form of an oil when added in considerable quantity.

With various acids, *e.g.* with hydrochloric, acetic, oxalic acid, &c., it forms compound ethers (Chancel).

Sulphopropylic or Sulphotritylic Acid. $C^6H^8O^2,2SO^3$. — Obtained in the form of a potash-salt by saturating with carbonate of potash a mixture of sulphuric acid and propylic alcohol diluted with water; evaporating to dryness over the water-bath; and exhausting the residue with boiling absolute alcohol. As the solution cools, the sulphotritylate of potash is deposited in delicate needles, which are anhydrous and very soluble in water.

				Chancel.
C^6H^7O,SO^3	91·0	....	51·07	
KO,SO^3	87·2	....	48·93	..... 48·4
$C^6H^8O^2,2SO^3$ or $C^6H^7\}2SO^4$	178·2	....	100·00	
$K\}$				

Propyloxanthic Acid. $C^6H^8O^2,2CS^2$. — The potash-salt of this acid, which crystallizes in slender needles, is obtained by adding bisulphide of carbon to a solution of potash in propylic alcohol (Chancel). ¶

Propylic or Propionic Aldide. $C^6H^6O^2$.

GUCKELBERGER (1847). *Ann. Pharm.* 64, 39.

Aldehyde of Propionic or Metacetonic Acid, [*Sixaldid, Nesixe*].

Passes over, together with many other products, in the distillation of casein, albumin, or fibrin, with sulphuric acid and peroxide of manganese, or with sulphuric acid and chromate of potash (VII, 127, 131).

Preparation. By distilling 1 pt. of dry casein with 3 pts. of peroxide of manganese, 4½ pts. oil of vitriol, and 30 pts. water.

The details of this process, to which it will often be necessary to refer, for the sake of the other products formed, are as follows: Skimmed milk is left to coagulate; the curd freed as completely as possible from the whey by washing with water and pressure; dissolved at 60° to 80° in dilute carbonate of soda; the solution maintained at that temperature for some hours; the scum thereby formed, carefully removed; the slightly turbid liquid precipitated by dilute sulphuric acid; the curd repeatedly stirred up with hot water, and the liquid each time pressed out of it, till the water runs away quite clear; and the resulting casein, which contains but a trace of fat, dried. — 4·5 pts. of oil of vitriol are diluted with 9 pts. water; the mixture cooled to 50° or 40°; 1 pt. of dry casein, pulverized as finely as possible, gradually added to it, with constant stirring, till, in the course of a few hours, it dissolves, and forms a brown or violet solution; and the remaining portion of fat, which then rises to the surface, skimmed off. The solution is left to stand for a day, because it afterwards distils more easily, and yields a greater quantity of volatile products; then diluted with 10 pts. water, and introduced into a retort large enough to hold twice the quantity; 11 pts. of water added (making up the 30); the liquid distilled into a well cooled receiver, as long as any odoriferous products pass over; 1½ pts. more manganese introduced into the retort, together with a quantity of water equal to that which has already passed over; and the liquid again distilled as long as the distillate has any odour.

The strongly acid distillate (which is clouded by a few white flakes, and the first portion of which has a very pungent odour and excites tears and coughing, while the latter portions have an odour of bitter almond oil), is neutralized with chalk, and distilled to one-half; the resulting distillate—which is neutral at first, but soon turns acid on exposure to the air, exhibits the reactions of aldehyde, and contains aldehyde, propylic aldide, butyral, and bitter almond oil—redistilled into a well cooled receiver, collecting only the first portion which passes over, till this distillate presents the appearance of a milky water covered with yellow oil, becoming clear as it cools, and gradually depositing bitter almond oil. It now remains to separate the propylic aldide from the more volatile aldehyde, from the less volatile butyral and bitter almond oil, and from water. To effect the first-mentioned separation, the milky liquid is introduced into a retort or a flask, to which is adapted a long tube slanting upwards at first, and afterwards conveying the vapours into the downwardly inclined condensing apparatus, and heated in the water-bath,

at first only to 40° or 50°, at which temperature nothing but aldehyde passes over, whilst the propylic aldide condenses in the upwardly inclined tube, and flows back again. The propylic aldide is then distilled over at 65° to 70°, the first portions still containing aldehyde, whilst the last portions, which must be collected apart, are free from that impurity, and have a pleasant ethereal odour (at a higher temperature the butyral passes over, and above 100°, the bitter almond oil). The distillate collected between 65° and 75° is dehydrated over chloride of calcium, and distilled in a retort provided with a thermometer, whereupon it begins to boil at 40°. The distillate collected between 50° and 70° is tolerably pure propylic aldide, not however exhibiting a perfectly constant boiling-point.

After the aldides have been distilled off, there remains in the retort a solution of formiate, acetate, propionate, butyrate, valerate, caproate, and benzoate of lime. These lime-salts are converted into soda-salts by precipitation with carbonate of soda; the precipitate further evaporated, so as to obtain by repeated cooling, crystals of acetate and formiate of soda; the no longer crystallizable mother-liquor mixed with sulphuric acid; the brownish oily mixture of butyric, valeric, and benzoic acid, which rises to the surface, taken off; the butyric acid removed from it by repeated agitation with an equal quantity of cold water; the valeric acid distilled, the benzoic acid subliming at the same time; the mother-liquor obtained by decomposing the soda-salts with sulphuric acid, decanted from the sulphate of soda, and mixed with the wash-water containing the butyric acid; and this mixture neutralized with carbonate of soda, evaporated to dryness in the water-bath, and again decomposed by dilute sulphuric acid. A nearly, colourless, oily acid mixture then remains, which when distilled by itself, begins to boil above 100°, yields propionic acid between 130° and 140°, and butyric acid between 160° and 165°, while an oily mixture of butyric, valeric, and caproic acid, boiling above 165°, remains in the retort.

Properties of Propylic aldide. Transparent, colourless liquid, of sp. gr. 0·79 at 15°; boils between 55° and 65°. Vapour-density = 2·111. Has a pleasant ethereal odour. Neutral.

			Guckelberger.	
			Boil. at 55° to 60°.	At. 60° to 65°.
6 C	36	62·07	61·90	62·18
6 H	6	10·34	10·39	10·63
2 O	16	27·59	27·71	27·19
C^6H^6,O^2	58	100·00	100·00	100·00

Metameric with acetone. The calculated vapour-density is, like that of acetone, (p. 3) = 2·0105. According to the theoretical views of Williamson, Gerhardt, and Chancel, the formula of this body is $\left.\begin{matrix}C^6H^5O^2\\H\end{matrix}\right\}$, propionic acid being $\left.\begin{matrix}C^6H^5O^2\\H\end{matrix}\right\}O^2$.

Propylic aldide turns acid slowly when merely exposed to the air; but pretty quickly when in contact with platinum-black. The portion of the distillate which boils below 60° is not sensibly altered by potash, but the portion which boils above 60° is coloured yellow by it. Propylic aldide does not reduce nitrate of silver; it is therefore free from aldehyde (Guckelberger).

The quantity of this compound obtained by Guckelberger was not sufficient to enable him to demonstrate its difference from acetone with greater exactness.

Propionic Acid. $C^6H^6O^4$.

J. Gottlieb. *Ann. Pharm.* 52, 121.
Dumas, Malaguti & Leblanc. *Compt. rend.* 25, 656 and 781.
Redtenbacher. *Ann. Pharm.* 57, 174.
F. Wrightson. *Phil. Mag.* [4], 6, 88; *Ann. Pharm.* 90, 36; *Jahresber.* 1853, 438.

Metacetic or *Metacetonic acid, Metacetsäure, Metacetonsäure, Acide métacétonique, Acide propionique.* Discovered by Gottlieb in 1844.

¶. *Sources.* In crude oil of amber, whence it may be obtained, together with other volatile fatty acids, by distillation with water (Marsson, *Arch. Pharm.* [2], 62, 1; *Jahresber.* 1850, 494). — 2. In cocoa-nut milk after it has turned sour (Löwenich, *Jahrb. pr. Pharm.* 24, 218; *Jahresber.* 1852, 678). — 3. In the distillate obtained from a thin sort of wine from the Bergstrasse (Winckler, *Jahrb. pr. Pharm.* 26, 209; *Jahresber.* 1853, 438). ¶.

Formation. 1. By heating cyanide of ethyl (VIII, 486) with potashley (Dumas, Malaguti & Leblanc, *Compt. rend.* 25, 656; Frankland & Kolbe, *Phil. Mag. J.* 31, 266; also *Ann. Pharm.* 65, 300; also *J. pr. Chem.* 42, 313):

$$C^4NH^5 + 3HO + KO = C^6H^5KO^4 + NH^3.$$

Cyanide of ethyl is also decomposed by distillation with a mixture of 1 pt. oil of vitriol and 2 pts. water, yielding sulphate of ammonia and a distillate of propionic acid (Frankland & Kolbe):

$$C^4NH^5 + 4HO + SO^3 = C^6H^6O^4 + NH^3,SO^3.$$

2. In the oxidation of metacetone by chromate of potash and sulphuric acid (Gottlieb; vid. *Metacetone*). — 3. By heating common sugar, mannite, starch, or gum with concentrated potash (Gottlieb). — 4. By exposing an aqueous solution of glycerine mixed with yeast to the air (Redtenbacher). Apparently also when glycerine is exposed to the air in contact with platinum-black (Döbereiner). — 5. When oleic acid is distilled with nitric acid, a moderate quantity of propionic acid is formed, together with many other volatile acids (Redtenbacher, *Ann. Pharm.* 59, 41: vid. *Oleic acid*). — 6. In the distillation of casein or fibrin with peroxide of manganese and dilute sulphuric acid (Guckelberger, pp. 400, 401); also of vegetable fibrin (F. Keller, *Ann. Pharm.* 72, 24). — 7. In the putrefaction of peas or lentils under water, butyric acid being formed at the same time (Böhme, *J. pr. Chem.* 41, 278). — 8. In the dry distillation of beeswax (Polock). — ¶. 9. In the oxidation, by nitric acid, of the more volatile distillation-products of rape-oil (F. C. Schneider, *Ann. Pharm.* 70, 107). — 10. In the oxidation of oil of turpentine by nitric acid (Schneider, *Wien Akad. Ber.* 1849, 337). — 11. From the volatile oil of *Asa fœtida*: *a.* By distilling the oil with water, the aqueous distillate containing propionic and valeric acids. — *b.* By heating the crude oil to 200°, sulphuretted hydrogen being then evolved, and the same two acids being found in the residue. — *c.* By oxidizing the crude oil with

nitric acid, in which case acetic and oxalic acid are likewise formed, — or by chromic acid, which likewise yields acetic acid (Hlasiwetz, *Ann. Pharm.* 71, 23). — 12. Oil of mustard oxidized by chromic acid, yields a large quantity of acetic, and a small quantity of propionic acid (Hlasiwetz). — 13. By the fermentation of citrate of lime, induced by contact with decaying cheese: this process yields sometimes a mixture of acetic and propionic acid, sometimes only acetic acid (H. How, *Chem. Soc. Qu. J.* V, 1). — 14. By the fermentation of bran induced by contact with leather (F. Keller, *Ann. Pharm.* 73, 205). The formation of propionic acid in this manner is denied by Forster (*Chem. Soc. Qu. J.* V, 28). — 15. By the fermentation of sugar in contact with chalk and old cheese. — A mixture of this kind (prepared according to Bensch's directions for the formation of lactic acid), having been left during winter in a room which was heated during the day only, deposited crusts of lactate of lime after the lapse of two or three months (in a warm place this effect taken place in 8 or 10 days); when concentrated by evaporation, it yielded more lactate of lime and crystals of mannite; and when subsequently left for some months during summer in a place whose temperature did not exceed 20° or 22°, the water being renewed as it evaporated, large quantities of propionic and acetic acids were formed, but no butyric acid. The two acids were separated by partial saturation with potash and distillation, the propionic acid passing over first, and the acetic acid remaining in the residue* (Strecker, *Compt. rend.* 39, 49; *Chem. Soc. Qu. J.* 7, 276). ¶

Preparation. Cyanide of ethyl is added by drops to moderately strong potash-ley heated in a tubulated retort; the distillate repeatedly poured back till it no longer smells of cyanide of ethyl, but only of ammonia; and the propionate of potash which remains in the retort, distilled with syrupy phosphoric acid. The propionic acid which passes over towards the end of the process is crystalline (Dumas, &c.). Frankland & Kolbe used sulphuric acid instead of phosphoric. — ¶. The cyanide of ethyl required for this process may be advantageously obtained by decomposing cyanide of potassium with iodide of ethyl. Crude iodide of ethyl is mixed with about four times its volume of alcohol, and the mixture introduced into a flask containing more than an equivalent quantity of cyanide of potassium. The flask is connected with a Liebig's condenser, in such a manner that when it is heated in the water-bath, the condensed vapours may flow back again. A few drops of liquid are taken out from time to time by inclining the apparatus, and tested for iodine with boiling alcoholic potash. As soon as the reaction is complete, the liquid is distilled to dryness, and the saline residue washed by distilling a little alcohol over it. The distilled liquid is then decomposed by potash as above, for which process also the apparatus just described may be conveniently employed; it is advisable also to connect the condenser with one or two Woulfe's bottles to absorb the ammonia (Williamson, *Phil. Mag.* [4], 6, 205). ¶.

2. Metacetone is introduced into a mixture of dilute sulphuric acid and chromate of potash contained in a capacious retort, and distilled

* When a mixture of acetic acid with propionic, butyric, or valerianic acid is partially neutralized with potash and distilled, the acetic acid, although the most volatile, always remains in the residue in preference to the others, apparently in consequence of the formation of an acid acetate, which is not decomposed by either of the other acids (Liebig, *Ann. Pharm.* 71, 355).

after the effervescence caused by the formation of carbonic acid has ceased. Undecomposed metacetone passes over first, then a mixture of propionic and acetic acids, which must be collected in a separate receiver. This mixture is neutralized with carbonate of soda, and evaporated till the greater part of the acetate of soda crystallizes out; and the thick mother-liquor, which yields no more crystals, diluted with water and left to evaporate slowly, whereupon acetate of soda again crystallizes out. The mother-liquor thus freed from the greater portion of this salt, is then distilled with sulphuric acid (Gottlieb).

3. Potash-ley is concentrated so far that it would solidify on cooling, and common sugar introduced into it (about 1 pt. sugar to 3 pts. hydrate of potash) the heating being continued all the time. The mixture turns brown and continually gives off hydrogen, first with the odour of caramel, afterwards with a more aromatic odour; becomes viscid in a few minutes, still continuing to froth; then loses its colour and becomes tolerably solid. The fire is now removed; the pale yellow saline mass dissolved when cold in a small quantity of water; the solution supersaturated, gradually so as to avoid great rise of temperature, with moderately dilute sulphuric acid, which causes a great evolution of carbonic acid; then filtered, acid oxalate of potash remaining on the filter; distilled; the distillate containing formic, acetic, and propionic acid, boiled with excess of mercuric oxide as long as carbonic acid continues to escape, to destroy the formic acid; the mercury removed from the filtrate by sulphuretted hydrogen; and the filtrate containing acetic and propionic acids treated with carbonate of soda, &c., as in (2). The product is but small. (Gottlieb).

4. A solution of glycerine in a large quantity of water is mixed with well washed yeast, and exposed to the air for several months at 20° to 30°, the water being occasionally renewed, and the liquid frequently stirred to divide the yeast which rises to the surface, and aggregates in fungoïd masses; the acid as it forms is frequently neutralized, till the liquid no longer turns sour; after which it is evaporated, and the saline mass distilled with dilute sulphuric acid. The acid thus obtained is somewhat contaminated with acetic and formic acid.

5. Casein is distilled with manganese and dilute sulphuric acid (Guckelberger, pp. 401, 401).

6. Lentils or peas immersed in water are exposed to the sun; the putrefied mass distilled with sulphuric acid, which retains the ammonia; the distillate saturated with carbonate of baryta, &c. The propionic acid thus obtained is contaminated with butyric acid, especially when peas are used (Böhme).

¶. Wheat-bran is stirred up with 10 times its weight of water at 50° or 60°, to a pasty consistence; mixed with a fourth of its weight of coarsely cut leather parings; pounded chalk added; and the mixture left to ferment in a warm place. As soon as the tumefied spongy mass has sunk together (an effect which takes place in a few days in summer, but only after several weeks in winter), it is strained and washed; the liquid saturated with carbonate of soda and evaporated; and the acid which has formed, separated from the residue by sulphuric acid. On partially saturating the resulting acid with carbonate of soda and distilling, a residue is obtained consisting of acetate and propionate of soda. No other acid appears to be formed (Keller). — R. W. Forster, in repeating this process, did not obtain any propionic acid, though he left the mixture in a warm place for three weeks; the acid which formed appeared to him to be chiefly formic acid.

8. Propionic acid may also be obtained in considerable quantity by the fermentation of sugar induced by old cheese (Strecker, p. 403). ¶

Properties. The acid dehydrated as completely as possible, crystallizes in laminæ and boils at 140° (Dumas, &c.). The aqueous acid smells of butyric and acrylic acid together, and tastes very sour (Gottlieb).

Calculation.

6 C	36	....	48·65
6 H	6	....	8·11
4 O	32	....	43·24
$C^6H^6O^4$	74	....	100·00

¶. According to Williamson and Gerhardt, the formula of the hydrated acid is $\left.\begin{matrix}C^6H^5O^2\\H\end{matrix}\right\}O^2$; according to Kolbe, it contains ethyl conjugated with 2 At. C, and its formula is $HO,(C^4H^5)C^2,O^3$. ¶.

Combinations. The acid dissolves in water in all proportions (Dumas, &c). Water dissolves only a certain quantity of it, the excess of the acid floating on the water in oily drops (Redtenbacher). On the surface of aqueous phosphoric acid or solution of chloride of calcium, it floats in the form of an oily stratum (Dumas, &c.).

The *Propionates*, when heated alone, emit an odour like that of alkarsin, and when heated with dilute sulphuric acid, give off the odour of propionic acid; they are soluble in water and most of them are crystallizable. According to Dumas, &c., the alkaline propionates are unctuous to the touch.

Propionate of Ammonia. — Converted by anhydrous phosphoric acid, with loss of water, into cyanide of ethyl (= propylonitrile) (Dumas, &c.):

$$NH^3,C^6H^6O^4 = C^6NH^5 + 4HO.$$

Propionate of Potash. $C^6H^5KO^4$. — White, with pearly lustre, unctuous to the touch, very soluble in water (Dumas, &c.) Thin laminæ (Strecker).

Propionate of Soda. — $C^6H^5NaO^4 + 2Aq$. — Very soluble in water, and apparently uncrystallizable (Dumas, &c.). — When dried in the air it forms an amorphous mass (Strecker).

Aceto-propionate of Soda. — The preparation of this salt succeeded only once. Delicate shining needles, very easily soluble in water. They lose 30·55 (9 At.) water by drying, and the dry salt contains 35·13 p.c. soda. Hence the crystals $= C^6H^5NaO^4 + C^4H^3NaO^4 + 9Aq$. (Gottlieb).

Propionate of Baryta. — Segments of regular octohedrons, very easily soluble in water (Böhme). [Respecting the crystalline form, *vid.* Prevostaye *Compt. rend.* 25, 782]. Yields propione, $C^{10}H^{10}O^2$, by dry distillation (Morley, p. 409).

	Crystals.				Böhme.		Frankland & Kolbe.		Wrightson.
BaO	76·6	....	54·10	.....	54·10	.....	53·65	.....	53·30
6 C	36·0	....	25·42	.....	23·40	.....	24·98		
5 H	5·0	....	3·53	.....	3·66	.....	3·79		
3 O	24·0	....	16·95	.....	18·84	.....	17·58		
$C^6H^5BaO^4$	141·6	....	100·00	.....	100·00	.....	100·00		

Wrightson's salt was purified by recrystallization, and dried at 100°.

¶ *With* 1 *At. Water.* The aqueous solution yields by spontaneous evaporation, large, beautiful and very regular prismatic crystals containing 1 At. water of crystallization, which is driven off at 100°. (Wrightson).

				Wrightson.
BaO	76·6	....	50·86	
6 C	36·0	....	23·90	
5 H	5·0	....	3·32	
3 O	24·0	....	15·94	
HO	9·0	....	5·98	..... 5·97
$C^6H^5BaO^4 + Aq$	150·6	....	100·00	

Strecker likewise obtained crystals belonging to the rhombic system, containing 1 At. water, and soluble in 1·3 pt. water at 15°.

Propionate of Lime. — Obtained by neutralizing an aqueous solution of propionic acid with recently precipitated carbonate of lime. Crystallizes by spontaneous evaporation in long and very beautiful prisms which unite in tufts. Not altered by exposure to the air, and even when dried over sulphuric acid, it retains 1 At. water of crystallization, which does not go off till the salt is heated to 100° (Wrightson).

Anhydrous.				Wrightson.
CaO	28	....	30·11	..... 30·4
6 C	36	....	38·71	
5 H	5	....	5·38	
3 O	24	....	25·80	
$C^6H^5CaO^4$	93	....	100·00	

Crystallized.				Wrightson.
CaO	28	....	27·45	
6 C	36	....	35·30	
5 H	5	....	4·90	
3 O	24	....	23·53	
HO	9	....	8·82	..... 8·8
$C^6H^5CaO^4 + Aq$	102	....	100·00	

Strecker also obtained the anhydrous salt $C^6H^5CaO^4$ in silky pallets. ¶

Propionate of Lead. — The solution, which has a sweet taste, dries up without yielding crystals, to a white mass, which when dried at 100° contains 63·4 p.c. oxide of lead (Frankland & Kolbe). — ¶ Needles composed of $2PbO,C^6H^5O^3$ [$PbO,C^6H^5PbO^4$] (Strecker). This formula requires 77·51 p.c. PbO.

Chloride of barium added to a tolerably concentrated solution of propionate of lead, forms at first a somewhat copious precipitate which disappears by agitation; if the addition of the chloride be continued, a point is at length attained at which the precipitate no longer redissolves; if the liquid be then filtered, and left to evaporate, chloride of lead separates at first, and afterwards magnificent limpid crystals which appear to belong to the tetragonal system. They dissolve readily in water, and produce gyratory movements on the surface of that liquid. They contain 4·15 to 3·88 p.c. chlorine, 35·96 to 35·70 lead, and 24·32 to 24·2 barium (Nickles, *Ann. Pharm.* 61, 843).

Propionate of Copper. — Obtained by neutralizing the aqueous acid with carbonate of copper. Very regular green octohedrons, sometimes with cube-faces. Dissolves in water with tolerable facility, and is easily obtained in crystals by spontaneous evaporation. The crystals dried over oil of vitriol retain 1 At. water, which goes off at 100° (Wrightson). —Crystallizes in small oblique prisms very soluble in alcohol but very sparingly in water. Heated to 100° in a current of dry air, it gives off its water, together with a certain quantity of propionic acid. If from this point the temperature be suddenly raised to dull redness, the decomposition proceeds rapidly, with evolution of combustible gases which carry away a portion of the salt. The products of this distillation are: an odoriferous liquid composed of propionic acid and an oily body insoluble in water; carbonic acid and a hydrocarbon; and a residue of metallic copper and charcoal (Nicklès, *Compt. rend.* 1849, 348).

Anhydrous.			Wrightson.
CuO	40	38·09	37·68
6 C	36	34·29	
5 H	5	4·76	
3 O	24	22·86	
$C^6H^5CuO^4$	105	100·00	

Crystallized.			Wrightson.	Nicklès.
CuO	40	35·09		
6 C	36	31·58		
5 H	5	4·39		
3 O	24	21·05		
HO	9	7·89	7·9	
$C^6H^5CuO^4 + Aq$	114	100·00		

Strecker likewise obtained the hydrated salt, $C^6H^5CuO^4 + Aq$. in green crystals probably isomorphous with the acetate. ¶

Propionate of Silver. — Obtained by adding nitrate of silver to the concentrated aqueous solution of the soda-salt as long as a precipitate is formed; boiling the precipitate in the liquid till it dissolves, whereupon some of the silver is reduced; and filtering at the boiling heat: the liquid on cooling yields white, shining, heavy granules, which when examined by the microscope are found to consist of geodes of needles. A few more crystals may be obtained by evaporating the mother-liquor. The salt when merely exposed to light, remains unaltered for several weeks; but at 100°, it suffers partial decomposition and becomes black-brown. At a higher temperature, it melts quietly and burns away without noise (Gottlieb). — The white crystalline precipitate obtained by treating the potash-salt with nitrate of silver, crystallizes from its hot aqueous solution in delicate, shining tufts (Dumas, Malaguti & Leblanc). — When the precipitate is dissolved in boiling water, the greater part of it decomposes; and the crystals obtained from the solution decompose when heated, giving off acid vapours (Guckelberger). — Small crystalline laminæ, which, either in the dry state or in solution, blacken when exposed to light or heated to 100°. Less soluble in water than the acetate (Frankland & Kolbe).

Crystallized, dried in vacuo.			Frankland & Kolbe. (1)	Gottlieb. (2)	Gottlieb. (3)	Redtenbacher. (4)	Morley.
AgO	116	64·09	64·29	64·00	63·83	64·63	64·31
6 C	36	19·89	19·78	19·76	19·74	19·89	
5 H	5	2·76	2·68	2·80	2·78	2·70	
3 O	24	13·26	13·25	13·44	13·65	12·78	
$C^6H^5AgO^4$	181	100·00	100·00	100·00	100·00	100·00	

The numbers (1), (2), (3), and (4) refer to the modes of preparation of the acid used in forming the silver-salt.

Aceto-propionate of Silver. $C^{10}H^8Ag.^2O^4$. — When a solution containing both propionate and acetate of soda is heated to the boiling point with nitrate of silver and filtered hot, the double salt crystallizes on cooling, in shining dendrites loosely coherent when dry. If the salt be decomposed by aqueous chloride of sodium, the filtrate yields by evaporation crystals of acetate of soda (Gottlieb). The crystals do not melt at a higher temperature (Guckelberger). They dissolve sparingly in water, and the solution turns black or brown at a boiling heat, and yields reduced silver (Frankland & Kolbe; Poleck).

¶ Acetopropionic acid is also produced by the fermentation of citrate of lime in contact with putrefying curd. When crystallized citric acid powdered and made up into a thin paste with excess of chalk and water, is mixed with a fourth of its weight of curd, the mixture diluted with ten times its bulk of water, and set aside in a warm place, carbonic acid and hydrogen gases are evolved, and in about three weeks an acid liquid is obtained, which, when neutralized with carbonate of soda, filtered, evaporated, and distilled with sulphuric acid, yields, first aceto-propionic and afterwards acetic acid.—The first portion of the distillate, neutralized with ammonia and treated with nitrate of silver, yielded a copious white flocky precipitate which dissolved in water with partial decomposition and blackening, but nevertheless formed a solution which deposited acetopropionate of silver (*a*) in white rounded granules, presenting under strong magnifying power the appearance of sasifrage or lycopodium. It was not affected by light but was speedily blackened at 100°. — Another portion of the first distillate was saturated with carbonate of lead, and the solution evaporated to a syrup, which solidified in an opaque, crystalline mass on cooling; this, when distilled with strong sulphuric acid, yielded a pungent acid liquid, which, when neutralized with carbonate of soda and treated with nitrate of silver, yielded a salt (*b*) similar in external character to *a* (How, *Chem. Soc. Qu. J.* 5, 1). ¶

Crystallized.			Gottlieb.	Guckelberger.	Poleck.	Redtenbacher.	How. *a.*	How. *b.*
2 AgO	232	66·67	66·43	67·06	64·75	66·87	66·70	67·13
10 C	60	17·24	17·45		16·87	17·64	16·63	17·07
8 H	8	2·30	2·40		2·45	2·23	2·51	2·38
6 O	48	13·79	13·72		15·93	13·26	14·16	13·22
$C^6H^5AgO^4,C^4H^3AgO^4$	348	100·00	100·00		100·00	100·00	100·00	100·00

¶ How's salts were dried in vacuo. The latter portion of the distillate obtained by the fermentation of citrate of lime, as above described, was found to consist of acetic acid. In a second experiment of the same kind, with slightly varying circumstances, nothing but acetic acid was obtained (How). ¶

Conjugated Compound of Propionic Acid.

Propionate of Ethyl. $C^{10}H^{10}O^4 = C^4H^5O, C^6H^5O^3$.

GOTTLIEB. *Ann. Pharm.* 52, 126.

Propionic Ether, Metacetic Ether, metacetsäures Aethyloxyd, Ether metacétique.

When propionate of silver is boiled with a mixture of absolute alcohol and oil of vitriol, and water added, propionic ether rises to the surface, in the form of a light liquid, having an agreeable fruity odour, but different from that of butyric ether (Gottlieb).

Propionic ether in contact with aqueous ammonia is quickly converted into propionamide (metacetamide) and alcohol (Dumas, Malaguti, & Leblanc).

Propione. $C^{10}H^{10}O^2 = C^4H^4, C^6H^6O^2 = \left.\begin{matrix} C^6H^5O^2 \\ C^4H^5 \end{matrix}\right\}$

FREMY. *Ann. Chim. Phys.* 59, 6; also *Ann. Pharm.* 15, 278; also *J. pr. Chem.* 5, 347.
GOTTLIEB. *Ann. Pharm.* 52, 127.
CHANCEL. *Compt. rend.* 20, 1582 and 21, 908.
R. J. MORLEY. *Chem. Soc. Qu. J.* 4, 1; *Ann. Pharm.* 78; 187; abstr. *Pharm. Centr.* 1851, 524; *J. pr. Chem.* 53, 179; *N. J. Pharm.* 19, 391; *Jahresber.* 1851, 437.

Metacetone, Metaceton. — Discovered by Fremy in 1835. — Sometimes found in crude wood-spirit (Cahours, p. 56).

Formation. 1. In the distillation of sugar, starch, gum (Fremy) or mannite (Favre), with excess of lime. — The first product is probably propionate of lime, which at a higher temperature is resolved into carbonate of lime, water, and propione (Chancel):

$$2C^6H^5CaO^4 = 2(CaO,CO^2) + C^{10}H^{10}O^2.$$

2. By the distillation of lactate of lime (Favre, *N. Ann. Chim. Phys.* 11, 80). — 3. By the distillation of propionate of baryta (Morley).

Preparation. 1. An intimate mixture of 1 pt. sugar, starch, or gum with 8 pts. of burnt lime, is gently heated in a retort large enough to hold double the quantity, and the fire removed as soon as the lime becomes heated by the water evolved from the sugar, the heat thus developed being sufficient to continue and complete the distillation. The oily product which passes over is freed from the greater part of the acetone by agitation with water; the undissolved oil distilled at an increasing heat; and the receiver changed as soon as the liquid which passes over is no longer soluble in water, and consequently the greater part of the acetone has distilled over. The last distillate, after being several times briskly agitated with water, is again fractionally distilled, and set aside for three

days in contact with chloride of calcium; if it be then decanted and distilled, it yields pure propione (Fremy). — A larger quantity of propione is obtained by taking 1 pt. sugar to 3 pts. lime, and distilling in a still provided with a well cooled condensing tube (Gottlieb). — ¶ 2. Propionate of baryta subjected to dry distillation, which may be conveniently performed in Florence flasks (placed obliquely on a wire-gauze over a gas-burner) yields a brown liquid of not unpleasant odour, and changing to light yellow when dehydrated over chloride of calcium and rectified. Thus purified, it begins to boil at 80°; but the boiling point rapidly rises to 100°, and subsequently to 108°. By further rectification, a portion may be obtained which boils at 100°: this is the pure propione (Morley). ¶

Properties. Colourless oil boiling at 84° (Fremy). Colourless or pale yellow; boils at 100° (Morley). Has an agreeable odour (Fremy, Morley). Lighter than water (Morley).

Calculation, according to Fremy.			Fremy.
12 C	72	73·47	73·50
10 H	10	10·20	10·12
2 O	16	16·33	16·38
$C^{12}H^{10}O^2$	98	100·00	100·00

Calculation, according to Chancel.			Morley.
10 C	60	69·77	69·34
10 H	10	11·63	11·83
2 O	16	18·60	18·83
$C^{10}H^{10}O^2$	86	100·00	100·00

Fremy's calculation agrees best with his own analysis; but Chancel's calculation, according to which propione is a ketone (VII, 214) is by far the more probable of the two. ¶ Moreover, Chancel's calculation agrees best with Morley's analysis, which, being of recent date, is much more reliable than Fremy's, the latter having been made at a time when the methods of organic analysis were very imperfect.

Decompositions. Propione is very inflammable and burns with a pale blue flame without deposition of carbon (Morley). — 2. It is oxidized by fuming or boiling nitric acid, yielding propionic acid, but no nitropropionic or acetic acid (Morley). ¶ — Nitric acid converts propione into nitropropionic acid (Chancel). — 2. By sulphuric acid and bichromate of potash, it is converted, with rise of temperature and evolution of carbonic acid into propionic and acetic acids (Gottlieb). [If the carbonic acid be regarded as a result of oxidation carried too far, the decomposition may be expressed by the equation:

$$C^{10}H^{10}O^2 + O^6 = C^6H^6O^4 + C^4H^4O^4].$$

When propione is dropped upon hydrate of potash fused in a tubulated retort, it distils over for the most part unaltered, leaving mere traces of propionic acid in combination with the potash. Similarly with a mixture of lime and hydrate of potash (Gottlieb).

Combinations. Propione is insoluble in water, but dissolves readily in alcohol and ether (Fremy, Morley).

¶ **Propylamine.** $C^6H^9N = C^6H^6,NH^3 = \left.\begin{matrix} C^6H^7 \\ H \\ H \end{matrix}\right\}N.$

Tritylamine, Metacetamine, Oenylamine. — This base, or one metameric with it, was first obtained by Wertheim in 1850. It is obtained: 1. By distilling *narcotine* at 220° to 250° with potash-lime or soda-lime (Wertheim, *Ann. Pharm.* 73, 208). — 2. By distilling *codeine* at 120° to 175°, with potash or soda-lime. Ammonia is then evolved, and a watery liquid distils over, which has a peculiar pungent odour; and when distilled with hydrate of potash, yields, besides ammonia and a small quantity of a basic crystalline body, two volatile bases, viz. gaseous methylamine, and propylamine in the form of an oily liquid (Anderson, *Edinb. Phil. Trans.* 20, I, 557; *Chem. Gaz.* 41, 68; *Ann. Pharm.* 77, 341; *Jahresber.* 1850, 420). — 3. From *bone-oil.* When the rectified oil was shaken up with sulphuric acid and distilled (to separate the pyrrol-bases) the residue treated with slaked lime and distilled to separate the bases which had been retained by the acid, a watery liquid passed over, from which, by the addition of solid hydrate of potash, the bases were separated as an oily layer. This oil, when fractionally distilled, yielded several bases, the most volatile of which, boiling below 65°, was propylamine (Anderson, *Edinb. Phil. Trans.* 20, II, 247; *Phil. Mag.* [4], 2, 257; *Chem. Soc. Qu. J.* 5, 50). — 4. From the brine of salted herrings (see page 413) by distillation with potash (Wertheim, *Wien Akad. Ber.* 6, 113; *J. pr. Chem.* 53, 435; *Jahresber.* 6, 113; *J. pr. Chem.* 53, 43; *Jahresber,* 1851, 480). — 5. From *Chenopodium vulvaria* (*stinking goosefoot, Chenopodium olidum*), by distillation with dilute potash or carbonate of soda (Dessaignes, *Compt. rend.* 33, 358; *Ann. Pharm.* 71, 106). — 6. From the flowers of the white thorn (*Cratægus oxyacantha*), by distillation with dilute soda or potash. It exists most abundantly in the half-developed buds, and gradually volatilizes as the flower expands; also, according to Wittstein, in the flowers of *Cratægus monogyna, Sorbus aucaparia,* and *Pyrus communis* (W. Wicke, *Ann. Pharm.* 91, 121). — 7. From *ergot of rye* (*Secale cornutum*) by distillation with quicklime or potash-lime (Walz, *Jahrb. pr. Pharm.* 24, 242; *Jahresber.* 1852, 552; Winckler, *N. Repert. Pharm.* 1, 116; *Jahresber.* 1852, 553. Winckler (*Jahrb. pr. Pharm.* 26, 129; *Jahresber.* 1853, 562) also treated ergot of rye pulverized and dried at 56°, first with ether, which extracted a fat oil, and then with water; mixed the aqueous extract with strong alcohol, which precipitated an albuminous substance; separated this precipitate by filtration; distilled off the alcohol from the filtrate; and evaporated the residue to dryness. The residue dissolved in alcohol and in water, with separation of a light brown powder; and when distilled with lime, yielded, not ammonia, but propylamine [or trimethylamine], Winckler regards the residue as consisting mainly of propylamine combined with ergotin. — In the flowers of *Cratægus,* &c., in the leaves of chenopodium, and in bone-oil, and herring-brine, the propylamine appears to exist ready formed; but that which is obtained from narcotine, codeine, and ergot of rye, by distillation with lime or potash-lime at high temperatures, is most probably a product of decomposition. — 8. Propylamine is also formed by the action of aqueous ammonia on iodopropylene C^6H^5I. (Berthelot & De Luca, p. 427.) [This is impossible, since iodopropylene contains only 5H].

Propylamine is a perfectly clear colourless liquid, having a strong,

pungent, and somewhat ammoniacal odour (Anderson); that which is obtained from narcotine has a fishy odour, like that of salted herrings (Wertheim). Forms a thick white cloud when a rod moistened with hydrochloric acid is held near it (Anderson). — Heated with nitrite of potash, it yields nitrite of propyl (Hofmann, *Chem. Soc. Qu. J.* 3, 231). It is soluble in water, and combines readily with acids.

Sulphate of Propylamine. — Dissolves readily in water and alcohol (Wertheim).

Hydrochlorate. — Crystallizes in large tables (Anderson). Dissolves readily in water and alcohol. The salt prepared with propylamine obtained from *Chenopodium* is deliquescent, and crystallizes from a very strong solution in elongated prisms. Its aqueous solution mixed with potash smells like salt cod or boiled crabs, and tastes like salt which has been used for salting cod (Dessaignes). Deliquescent, soluble in absolute alcohol (Berthelot & De Luca).

Gold-salt: — By mixing the solution of the hydrochlorate with terchloride of gold, the gold-salt is obtained in crystals resembling those of sal-ammoniac, and arranged in feathery groups (Dessaignes).

			Dessaignes.
6 C	36·0	8·99	
10 H	10·0	2·50	
N	14·0	3·49	
4 Cl	141·6	35·34	
Au	199·0	49·68	49·39
$C^6H^9N,HCl,AuCl^3$	400·6	100·00	

Platinum-salt. — Obtained by mixing the aqueous or alcoholic solution of the hydrochlorate with bichloride of platinum. Dissolves readily in cold water, still more in boiling water, sparingly in alcohol and ether, these liquids in fact precipitating it from its aqueous solution (Anderson). From the hot aqueous solution it crystallizes in beautiful golden-yellow scales (*a*), or in long needles (*b*), (Anderson); in extremely beautiful orange-yellow crystalline geodes (Wertheim).

		Dessaignes.	Anderson.		Wicke.
			a.	*b.*	
6 C	36·0	13·58	13·93	13·27	12·27
10 H	10·0	3·77	3·91	3·88	3·62
N	14·0	5·27	5·10		
3 Cl	106·2	40·05	40·50		
Pt	99·0	37·33	37·02	37·56	37·63	37·2
$C^6H^9N,HCl,PtCl^2$	265·2	100·00	100·46		

Anderson's salt *a* was prepared with propylamine obtained from bone-oil; *b*, with the base obtained by distilling codeine with soda-lime. The alkaline distillate obtained by the latter process was saturated with hydrochloric acid, evaporated to dryness, and treated with absolute alcohol, which left a large quantity of sal-ammoniac undissolved. The filtrate was mixed with an alcoholic solution of bichloride of platinum, and the precipitated double-salts dissolved in hot absolute alcohol, with addition of a small quantity of water. The liquid on cooling deposited pure chloroplatinate of methylamine (VII, 318). The mother-liquor was then evaporated and treated with ether, which threw down chloroplatinate of propylamine. The precipitate was partially purified by crystallization from water; but the quantity obtained was not sufficient to allow of its being completely freed from the methylamine-salt; consequently the amount of carbon came out too small and that of platinum too great. — Dessaigne's propylamine was obtained from *Chenopodium vulvaria;* Wicke's from the flowers of the white thorn.

As propylamine $(C^6H^7,H,H)N$, is metameric with trimethylamine, $(C^2H^3)^3N$, and with methylethylamine, $(C^2H^3),(C^4H^5),H,N$, the bases obtained from the several sources mentioned on page 411, may possibly be one or other of these methyl-compounds; for there is nothing in any of the characters above-mentioned that can serve to distinguish clearly between these and propylamine. — In the case of herring-brine indeed, it has been distinctly shown by Hofmann and Winkles (*Ann. Pharm.* 83, 116; *Chem. Soc. Qu. J.* 7, 63), that the base obtained is really trimethylamine; for when treated with iodide of methyl it yields iodide of tetramethylium (VII, 321). The same experiment made upon the bases obtained from the other sources above-mentioned would decide the question as to their nature. The fishy odour observed in more than one of them, seems however to indicate a connection with the methyl-compounds; moreover, Anderson's propylamine obtained both from bone-oil and from codeine, was actually associated with methylamine. Perhaps the base obtained from the flowers of the white-thorn and other plants of the same family, has the best right to be regarded as the real propylamine, inasmuch as the odour of those flowers is quite distinct from that of the methyl-bases, and has no fishy character.

¶ Arsenide of Propyl.

Wöhler. *Ann. Pharm.* 68, 127.

Arsenide of Trityl, Cacodyl of butyric acid.

When equal weights of butyrate of potash and arsenious acid, both well dried, are distilled together, a distillate is obtained consisting of two liquids, the upper nearly colourless, but the lower nearly black from the presence of metallic arsenic; this lower liquid, which does not mix with the upper, emits an odour like that of oxide of cacodyl. A large quantity of very stinking gas is at the same time evolved, and much arsenic is reduced.

When the entire distillate has been shaken up with water and magnesia, there passes over with the water a heavy colourless oil, which, as soon as it comes in contact with the air, becomes orange-yellow and ultimately dark-brown. This oil has a very offensive odour, like that of cacodyl, burns with a white flame, emitting an arsenical fume, but does take fire spontaneously or even fume on coming in contact with the air. When digested with strong hydrochloric acid, it acquires an odour which strongly irritates the eyes and nose.

The watery liquid which distils over together with this oil, appears to contain a considerable quantity of it in solution. When placed in contact with a solution of corrosive sublimate, it forms a nearly white precipitate, nearly losing at the same time its cacodylic odour, and acquiring an aromatic odour like that of butyrine. The precipitate dissolves when heated, and separates again in small crystals on cooling.

On mixing the entire liquid together with the precipitate with hydrochloric acid, and introducing some cuttings of zinc, the disagreeable cacodylic odour is soon reproduced, and the evolved hydrogen gradually acquires the property of diffusing copious white vapours in the air, and depositing an orange-coloured substance on cold bodies. On subjecting the mixture to distillation, a fetid oil passes over which fumes in the air, but does not take fire spontaneously (Wöhler). ¶

Appendix to Propionic Acid.

Pseudoacetic Acid.

Acide butyroacetique (Nicklès). This acid was discovered by Nöllner in 1841. Berzelius (*Jahresber.* 22, 233) pronounced it to be a mixture of butyric and acetic acid, and Nicklès regarded it as a conjugated compound of these two acids = $C^6H^6O^4 = C^{12}H^{12}O^8$. More recently, Dumas, Malaguti & Leblanc (*Compt. rend.* 25, 781) pronounced it to be identical with propionic acid, inasmuch as the two acids have the same crystalline form, boiling-point (140°) and odour; are equally soluble in water; and exhibit the same phenomena in contact with an aqueous solution of phosphoric acid or chloride of calcium; because also their salts emit the odour of alkarsin when heated, and their baryta-salts have the same crystalline form, with nearly the same angles. Notwithstanding the plausibility of this view, according to which, the discovery of propionic acid should be due, not to Gottlieb but to Nöllner, it must nevertheless be remembered that pseudoacetic acid exhibits many characters which in the case of propionic acid have certainly not been demonstrated, *e. g.* the separation into acetic and butyric acids; for the present, therefore, it is most convenient to keep the two acids separate. — The following are the statements of Nöllner and Nicklès respecting pseudoacetic acid.

Nöllner obtained pseudoacetic acid under the following circumstances: When crude tartar containing 20 per cent of fermentable matter, is neutralized with lime, the filtered tartrate of potash decomposed by boiling with sulphate of lime, and the tartrate of lime, after separation from the aqueous solution of sulphate of potash, left to itself, while still moist, on hot summer days, it ferments, and is converted, with copious evolution of carbonic acid, into a mixture of carbonate and pseudoacetate of lime, which, when distilled with sulphuric acid, yields pseudoacetic acid. — This acid was likewise produced in the fermentation of a mother-liquor of tartar containing a large quantity of tartrate of lime together with traces of nitrates. But tartrate of potash, either in the crude or the purified state, yields nothing but acetic acid: hence the formation of pseudoacetic acid appears to require the presence of lime.

The acid obtained by distilling the dry lead-salt with oil of vitriol, is colourless and smells of acetic acid; but after dilution in water, it acquires a pungent odour like that of old cheese.

All *pseudoacetates*, when thrown on water in small pieces, rotate rapidly upon it like camphor.

The *Potash-salt* crystallizes from the concentrated solution in long thin tables, and comports itself like acetate of potash.

Soda-salt. Small octohedrons, — or, if the aqueous solution be evaporated beyond the crystallizing point and then cooled, it forms a white, tallowy, amorphous mass; and if this be still further evaporated and then cooled, a radiated crystalline mass, which is less prone than the octohedrons to absorb water from the air, but is otherwise very easily soluble in water.

Baryta-salt. Threads united in tuft-like nodules.

Lime-salt. Resembles the acetate.

Magnesia-salt. Crystallizes readily from the concentrated solution in spherical aggregations of crystals.

Lead-salts. — *a. Perbasic.* — A boiling and very dilute solution of *b* mixed with ammonia, deposits on cooling a crystalline powder, which under the microscope, appears to consist, half of octohedrons, half of silky laminæ united in stellate groups.

b. Basic. — The aqueous solution of the salt *c* is boiled with protoxide of lead, filtered, and cooled to the crystallizing point; if the solution be dilute, and the temperature a few degrees above 0°, the crystalization is not complete in less than a week; the specific gravity of the mother-liquor is only 1·1075. — Large, transparent, colourless octohedrons. They remain unaltered in close vessels at ordinary temperatures, but effloresce in dry air. They melt even below 19° in their water of crystallization, which amounts to 42 per cent; hence the fusion takes place even on the hand, the crystals previously becoming turbid. If the deliquescence takes place slowly, it begins in the interior and extends outwards, nothing being ultimately left but a thin empty shell [consisting of salt which has lost its water by efflorescence] which retains the form of the crystals. — If the octohedrons be kept in the fused state for a while, or if the aqueous solution be brought to a state of higher concentration than that at which it yields the octohedrons, it expands in cooling and yields tables, containing less water, and therefore less easy to melt. Hence, on the occurrence of a change of temperature, the easily fusible salt may burst the vessel, by first melting, and then expanding as it solidifies. — A highly concentrated solution of the salt *b*, exposed to a low temperature for 12 to 24 hours, forms transparent spherical segments, which refract light strongly, and when placed on the warm hand, or otherwise gently heated, split up from the middle outwards, with a rustling noise like that of an electric spark, but without any appearance of light. The salt likewise dissolves very readily in alcohol, and separates out in needles united in stellate groups.

c. Neutral. — Crystallizes from the aqueous solution, at low temperatures only, in cauliflower-like aggregations, which contain but little water, melt, and give off a small quantity of water when heated, and deliquesce in very damp air.

The basic lead-salt *b* forms, with ferric oxide, a salt consisting of dark ruby-coloured needles united in spherical groups. The clear solution which it forms in cold water, deposits nearly all the ferric oxide when gently heated; but the oxide redissolves when left in the liquid for some time at ordinary temperatures. The ferric oxide in the salt amounts to only 1 per cent.

Copper-salt. — *a. Basic.* — Like verdigris. — *b. Neutral.* — Dark green hexagonal tables which easily fall to pieces.

Mercurous-salt. — Pearly scales which turn red and give off acid when exposed to the light.

Silver-salt. — Contains 61·3 p.c. oxide of silver; blackens quickly when exposed to light, and dissolves sparingly in water.

Pseudoacetic ether resembles acetic ether in odour and in other properties.

Thus far C. Nöllner (*Ann. Pharm.* 38, 299).

Nicklès examined the acid obtained by Nöllner and its lead-salt.

The acid was already decomposed into acetic and butyric acids, for it no longer formed the octohedral salt *b* with oxide of lead; when shaken up with chloride of calcium, it formed a layer of butyric acid, and below it a solution of chloride of calcium containing acetic acid; and after being neutralized with carbonate of ammonia, mixed at a boiling heat with nitrate of silver, and cooled, it finally yielded crystals of acetate of silver; and the mother-liquor, when subsequently evaporated, yielded this salt at first, but afterwards dendrites of butyrate of silver. This decomposed acid of Nöllner's does not precipitate basic acetate of lead. When saturated with carbonate of soda, it gives off carbonic acid, which at a certain time exhibits the odour of fermenting wine.

Nöllner's lead-salt, distilled with sulphuric acid, yields an acid which, when neutralized with baryta-water and evaporated, first yields rhombic tables, and then nodules of acetate of baryta.

But if the soda-salt be prepared [from the lead-salt ?], and decomposed by phosphoric acid, the pure pseudo-acetic acid rises to the top of the acid aqueous mixture in the form of an oily layer, and when decanted and rectified, exhibits the following properties:

Oily; boils at 140°; has a very persistent odour like that of perspiration.

Heated with oil of vitriol, it gives off sulphurous acid; and when heated with potash and arsenious acid, emits the odour of alkarsin.

With this pure acid, the following salts were prepared:

The *Potash* and *Soda-salts* are very deliquescent.

Baryta-salt. — Right rhombic prisms, having the four lateral edges truncated, and bevelled with two *y*-faces. The crystals smell like rancid butter, and are permanent in the air. Heated to 100° in a current of dry air, they lose 3·25 per cent of water; and at 200°, fuse and give off 2·8 p.c. more (in all, 6·05 p.c. = 1 At.); and if afterwards subjected to dry distillation, yield a non-acid oil, which is either a peculiar ketone [propione], or a mixture of acetone and butyrone. They dissolve readily in water, especially in hot water; very sparingly in absolute alcohol.

	Dried at 200°.			Nicklès.
BaO	76·6	....	54·10	54·14
6 C	36·0	....	25·42	25·62
5 H	5·0	....	3·53	3·46
3 O	24·0	....	16·95	16·78
$C^6H^5BaO^4$	141·6	....	100·00	100·00

Lime-salt. — Fibres, having a silky lustre, effloresing in the air, soluble in water.

	Dry.			Nicklès.
CaO	28	....	30·11	30·22
6 C	36	....	38·71	38·95
5 H	5	....	5·37	5·80
3 O	24	....	25·81	25·03
$C^6H^5CaO^4$	93	....	100·00	100·00

Zinc-salt. — Soluble in water; the solution decomposes when boiled.

The concentrated solution of the neutral *Lead-salt*, mixed with ammonia, soon deposits small rose-coloured needles of basic butyrate of lead.

Baryta and Lead-salt. — In a tolerably concentrated solution of the neutral lead-salt, chloride of barium produces a precipitate which at first disappears on agitation; as soon as it remains permanent on further addition of chloride of barium, the liquid is filtered, and left to evaporate spontaneously. At first chloride of lead crystallizes out, but afterwards transparent, colourless square prisms of the double salt. The crystals give off 2·59 p.c. water at 100°. They contain baryta and lead-oxide in equal numbers of atoms, and when ignited, leave the lead, partly in the form of oxide, partly as chloride. They dissolve readily in water. If particles of the salt happen to remain on the surface of the water, they exhibit the rotatory movements of the salts of butyric acid.

Copper-salt. — Oblique prisms. They give off water at 100°, and at 150° an additional quantity, together with a portion of the acid; if they be then suddenly heated to redness, they give off combustible gases, together with carbonic acid, a mixture of pseudo-acetic acid and an oil [propione ?] insoluble in water, and leave copper mixed with charcoal. — The crystals rotate upon water, and dissolve in it in very small quantity only, unless acetic acid be added; but they are very soluble in alcohol.

Silver-salt. — Dendrites, which change very quickly when exposed to light.

	Dried in vacuo over oil of vitriol.			Nicklès.
AgO	116	....	64·09	..... 64·05
6 C	36	....	19·89	..... 19·16
5 H	5	....	2·76	..... 3·35
3 O	24	....	13·26	..... 13·44
$C^6H^5AgO^4$	181	....	100·00	..... 100·00

The acid dissolves in *Alcohol* and in *Ether*.

Pseudo-acetic ether has a fruity odour (Jer. Nicklès, *Rev. scientif.*; abstr. *Ann. Pharm.* 61, 343; abstr. *Compt. rend.* 23, 419).

B. Secondary Series.

a. *Oxygen-nuclei.*

α. Oxygen-nucleus. $C^6H^4O^2$.

Pyruvic Acid. $C^6H^4O^6 = C^6H^4O^2,O^4$.

Berzelius. *Pogg.* 36, 1.
Völckel. *Ann. Pharm.* 89, 57; abstr. *Pharm. centr.* 1854, 289; *Jahresber.* 1853, 424.

Pyroracemic acid, Brenztraubensäure, Pyrotraubensäure.

Formation. By the dry distillation of racemic and tartaric acid.

Preparation. 1. Effloresced racemic acid is gradually heated to 220° in a tubulated glass retort placed on the sand-bath, and maintained at that temperature as long as anything passes over, the frothing over of

the mass being prevented, when necessary, by stirring it with a platinum wire introduced through the tubulure. The resulting yellow distillate is rectified in the oil-bath, a process which goes on but slowly, and leaves a brown syrup containing pyrotartaric acid. The pale yellow rectificate contains pyruvic and acetic acid, a small quantity of empyreumatic oil, and a trace of wood-spirit or something similar. It cannot be obtained colourless by repeated distillation, because, at each repetition of the process, a certain amount of decomposition takes place, carbonic acid being evolved, and a brown extract remaining. — Hence the rectificate must either be evaporated in vacuo over oil of vitriol to the consistence of a thick syrup, whereby the acid is freed from the volatile acetic acid and the greater portion of the water; — or saturated with recently precipitated and washed carbonate of lead; and the granular lead-salt washed, suspended in water, decomposed by sulphuretted hydrogen, and the filtrate evaporated in vacuo as above (Berzelius). The watery liquid filtered from the lead-salt still contains pyruvic acid, because this acid cannot be completely saturated with carbonate of lead at ordinary temperatures; the portion thus retained is still available (Berzelius). — ¶. 2. Tartaric acid heated over an open fire, yields a distillate consisting chiefly of pyruvic and acetic acids, together with aldehyde, acetone, and other substances. If the heat be strong and suddenly applied, the tartaric acid is resolved into acetic acid, carbonic acid, and carbonic oxide:

$$C^8H^4O^{10} = C^4H^4O^4 + 2CO^2 + 2CO;$$

but if the heat be moderate and slowly raised, the acid is resolved into pyruvic and carbonic acid:

$$C^8H^4O^{10} = C^6H^4O^6 + 2CO^2;$$

these two modes of decomposition may go on together. — On rectifying the distillate, the portion which passes over between 105° and 120°, consists chiefly of acetic acid; that between 130° and 180°, of pyruvic acid; and that between 180° and 190°, of pyruvic and pyrotartaric acid. To obtain the pyruvic acid in a state of purity, the portion which distils over between 140° and 180°, is collected apart, and subjected to repeated fractional distillation, till a liquid is obtained whose boiling point is confined between the limits of 165° and 170°. This liquid, which still contains a certain quantity of water arising from the decomposition of a small portion of pyruvic acid by the boiling, is separated therefrom by leaving it for some days in vacuo over strong sulphuric acid and solid caustic potash, till about a fourth part of the acid is evaporated, and the admixed water with it (Völckel). Tartaric acid distilled in contact with pumice-stone is also almost wholly resolved into carbonic and pyruvic acids; but the pyruvic acid is then also converted into the syrupy modification (*vid. inf.*) and afterwards decomposed. A similar result is obtained by distilling a neutral tartrate *per se* (Völckel). ¶

Properties. (1). Colourless or pale yellow, viscid syrup, which draws out into threads. May, for the most, be evaporated without decomposition. Inodorous at ordinary temperatures; but when heated, it has a pungent acid odour, somewhat like that of hydrochloric acid; tastes sharp and acid, leaving a somewhat bitter after-taste in the throat (Berzelius). — ¶. The acid prepared by (2) is a faintly yellowish liquid of sp. gr. 1·288 at 18°; boils at 165°; has a not very powerful odour, like that of acetic acid, and a burning taste. In the concentrated state, it volatilizes completely without decomposition when gently heated or left in vacuo; but when diluted with water, it becomes altered after a while, so that it afterwards leaves an acid syrup when evaporated. ¶

				Völckel.
6 C	36	....	40·91	..... 40·79
4 H	4	....	4·55	..... 4·73
6 O	48	....	54·54	..... 54·48
$C^6H^4O^2,O^4$	88	....	100·00	..... 100·00

The hypothetical anhydrous acid would be = $C^6H^2O^5 = p\ \dot{U}$.

Decompositions. The aqueous acid undergoes partial decomposition when distilled, even at the temperature of the water-bath (Berzelius, *vid. sup.*). ¶ The syrupy acid heated above 200°, gives off carbonic acid and yields a distillate of pyrotartaric acid $C^5H^4O^4$, the residue becoming more and more yellow (Völckel). — Pyruvic acid dissolves in sulphuric acid, with slight colouring and rise of temperature, and the solution, when heated, gives off carbonic and sulphurous acids. Pyruvic acid is not decomposed by hydrochloric acid. In cold strong nitric acid, it dissolves without perceptible decomposition; but on heating the liquid, a violent action takes place, attended with formation of oxalic acid; the same result is obtained on boiling the acid with nitric acid of ordinary strength (Vöckel). ¶ — Terchloride of gold and its compounds with other metallic chlorides, are not reduced by pyruvic acid in the cold, but completely when heated: the liquid which surmounts the shining metallic gold is itself free from gold, but has nevertheless a yellow colour. Monochloride and bichloride of platinum, on the contrary, are not reduced by the aqueous acid, even at a boiling heat (Berzelius).

Combinations. The acid mixes in all proportions with *Water*.

Pyruvic acid is stronger than acetic acid, expels the latter from its salts on evaporation, and precipitates from solutions of acetates, those bases with which it forms sparingly soluble salts. The *Pyruvates* are prepared by saturating the dilute acid with the base; if the acid is concentrated, partial decomposition takes place, attended with yellow or brown colouring. The salts in the anhydrous state are translucent, gummy substances; with water they are capable of forming crystals, provided the base has been dissolved in the acid without application of heat, and the solution evaporated at ordinary temperatures [provided also, according to Völckel, they have been prepared with the volatile modification of the acid]. The concentrated aqueous solution of these crystallizable salts may be boiled without alteration; but on boiling a dilute solution, the salt passes into the amorphous state, and afterwards remains as a gummy residue when the liquid is evaporated. The salts thus rendered amorphous cannot be brought back to the crystalline state (Berzelius). [According to Völckel, the acid separated from the salts is always in the syrupy modification (1), and if again united with bases yields only amorphous salts]. — The salts redden litmus, but do not taste sour. They assume a lemon-yellow colour at 100° to 120°, and orange-yellow at a higher temperature. In the dry state, they evolve little or no heat when mixed with oil of vitriol; on subsequent application of heat, they emit the odour of the acid, and above 100° give off a small quantity of the unaltered acid; but even at a temperature considerably below 100°, the greater part of the pyruvic acid is decomposed, the mass assumes a black-brown colour, and if then distilled in the sand-bath, yields a mixture of pyruvic and acetic acids. The aqueous solutions of the pyruvates are coloured deep red by a small quantity of ferrous

sulphate, and if somewhat concentrated, form a white precipitate in a few hours with cupric sulphate. Those pyruvates which are insoluble in water, dissolve for the most part in aqueous caustic alkalis, and partially also in alkaline carbonates. They dissolve sparingly in alcohol, the quantity dissolved being less as the alcohol is more anhydrous, and are insoluble in ether (Berzelius).

Pyruvate of Ammonia. — The aqueous mixture of the acid and base leaves by spontaneous evaporation, a yellow deliquescent mass, having an extremely bitter taste, and nearly insoluble in absolute alcohol.

Pyruvate of Potash. — The aqueous mixture evaporated in vacuo, leaves small crystalline scales which deliquesce in the air; but if boiled before evaporation, it leaves a fissured gummy residue, which becomes moist on exposure to the air.

Pyruvate of Soda. — *a. Neutral. Crystalline.* — Separates by cold evaporation, in large, flat, rectangular prisms, if the solution contains acetate of soda, but from a pure solution, in rectangular tables and long laminæ. The powder of the crystals feels like talc. The crystals are anhydrous and contain 28·25 per cent of soda. Their highly saturated, boiling solution solidifies on cooling, in a crystalline mass, from which the mother-liquor runs away. They dissolve very sparingly in boiling absolute alcohol, and do not separate out on cooling; in hydrated alcohol they dissolve more readily; nevertheless, the greater part of the salt is precipitated from its aqueous solution saturated in the cold, by alcohol of sp. gr. 0·833, whilst any acetate of soda that may be mixed with it remains in solution. — *β. Amorphous.* — The very dilute aqueous solution of *a*, heated to the boiling-point, leaves, when evaporated over oil of vitriol, a transparent colourless gum, and when evaporated by heat, a yellow gum, a few crystals of *a* also forming when the solution is exposed to the air.

b. Acid. — The crystals of the neutral salt triturated with the concentrated acid, form a translucent jelly, which dries up to a swollen mass; if from this mass the free acid be removed by alcohol, there remains a white, tumefied powder, which has a bitter and somewhat acid taste, reddens litmus strongly; and when dissolved and evaporated, leaves a white fissured mass.

Pyruvate of Lithia. — *a. Crystalline.* Crystalline grains, which are somewhat difficult of solution in water, and do not become amorphous when separated from a concentrated solution by boiling and hot evaporation. — *β. Amorphous.* A very dilute solution of *a* evaporated in the water-bath, leaves a hard colourless gum, more soluble in water than *a*.

Pyruvate of Baryta. — *a. Crystalline.* — Obtained by spontaneous evaporation of a solution of carbonate of baryta in the somewhat dilute acid. Large, broad, shining scales, which are permanent in the air, give off their 5·45 p.c. (1 At.) water of crystallization at 100°, and dissolve with tolerable facility in water. The precipitate formed by an alkaline carbonate does not dissolve in excess of the reagent. — *β. Amorphous* — The aqueous solution of *a*, if only gently heated, yields on evaporation a gummy residue, which, when dried in the air, contains 10·33 p.c. (2 At.) of water, and dissolves but slowly in water even at the boiling heat.

Pyruvate of Strontia. — *α. Crystalline.* — Prepared like the baryta-salt. Forms a mass consisting of fine, glimmering scales, which, when suspended in water, impart to that liquid their glimmering aspect. The scales contain 12 p.c. (2 At.) water; they are less soluble in water than the baryta-salt; from a solution saturated at a boiling heat, they separate out again on cooling. With alkaline carbonates, they behave like the baryta-salt. — *β. Amorphous.* — Colourless, translucent gum, which, when gently heated, gives off all its water, and becomes milk-white and fissured.

Pyruvate of Lime. — *α. Crystalline.* — Prepared like the baryta-salt. Crystalline grains. Behaves with alkaline carbonates like the baryta-salt. — *β. Amorphous.* The slightest heating of the aqueous solution, even by the hand, causes it to yield by spontaneous evaporation, a gum instead of crystalline grains.

Pyruvate of Magnesia. — Difficult to obtain in granular crystals, because it very easily passes into the gummy condition. With alkaline carbonates, it behaves like the baryta-salt.

Pyruvate of Yttria. — *α. Crystalline.* — A mixture of the concentrated solutions of pyruvate of soda and chloride of yttrium deposits in a few hours, white grains, which dissolve slowly in water. — *β. Amorphous.* — The aqueous acid saturated with recently precipitated hydrate of yttria, dries up into a clear, hard, saccharine gum; and this, when mixed with water, yields white flakes and forms a liquid which on evaporation again leaves a gummy residue. The precipitate formed by caustic alkalis or alkaline carbonates dissolves in excess.

Pyruvate of Glucina. — On treating the aqueous acid with excess of hydrate of glucina, an undissolved *basic* and a soluble *neutral* salt are produced; the latter remains, on evaporating the solution, in the form of a transparent, fissured, sweet-tasting gum, which is not precipitated by caustic alkalis or by alkaline carbonates.

Pyruvate of Alumina. — An excess of hydrate of alumina forms with the aqueous acid, in like manner, a gelatinous *basic* salt, and a solution of a *neutral* salt, which dries up to a permanently soft mass, and is not precipitated by caustic alkalis or alkaline carbonates.

Pyruvates of Ziconia and *Thorina.* — Soluble in water; not precipitated by ammonia.

Uranic Pyruvate. — Of a fine yellow colour; readily soluble in water.

Manganous Pyruvate. — *α. Crystalline.* — By spontaneous evaporation. Milk-white mass composed of fine scales, resembling the strontia-salt, even in the appearance which it presents when stirred up with water. Slowly soluble in cold, more readily in hot water. — *β. Amorphous.* — By evaporating the solution with the aid of heat. Gummy; easily soluble in water. If it has turned brown during the evaporation, which often happens, the coloured portion remains for the most part undissolved.

Pyruvate of Bismuth. — The elutriated and ignited oxide dissolves slowly in the aqueous acid. The solution yields by evaporation a viscid syrup, which tastes like other bismuth-salts, does not become turbid by

solution in water, and is not precipitated by caustic alkalis, alkaline carbonates, or sulphuretted hydrogen.

Pyruvate of Zinc. — *a. Crystalline.* — When carbonate of zinc is dissolved in the very dilute acid, the solution, as it becomes saturated, deposits a snow-white granular powder of *a*. When carbonate of zinc is dissolved in a stronger solution of the acid, heat is evolved, and the liquid assumes a yellow colour. The liquid decanted from the granular powder deposits by spontaneous evaporation a gummy acid salt, which is decomposed by water, with deposition of a large quantity of the pulverulent salt *a*. The powder *a* undergoes no alteration at 100°, but at a higher temperature, turns first yellow, then brownish yellow, and then gives off its water of crystallization, amounting to 18·37 p.c. (3 At.). The powder is sparingly soluble in water. 100 pts. of it yield 54·3 pts. of sulphate of zinc. — *β. Amorphous.* — A solution of zinc in tolerably warm dilute pyruvic acid leaves, when evaporated over the water-bath, a clear yellowish gum, easily soluble in water. — When zinc is dissolved in the cold dilute acid, a viscid mixture of *a* and *β* is produced, which, by evaporation over the water-bath, is wholly converted into *β*.

Pyruvate of Lead. — *a. Terbasic.* — $2PbO,C^6H^3PbO^6 + Aq$. — Obtained by treating the neutral salt *b* with dilute ammonia, washing the separated salt with water, in which it is slightly soluble, and drying it over oil of vitriol, so that it may not absorb carbonic acid.

b. Monobasic. — *a. Crystalline.* — Carbonate of lead recently precipitated and still moist, is gradually added to the aqueous acid, not quite to saturation; the liquid left to stand for 24 hours above the precipitated salt, and frequently stirred to decompose any carbonate of lead that may still remain; and the heavy granular powder washed and dried. — Or the pyruvic acid is added to a concentrated aqueous solution of neutral acetate of lead, which remains clear at first, but after a few hours, thickens to a mass of the consistence of gruel, from which the salt *a* is deposited as a granular powder; it must then be washed and dried without heat. — The salt dried in the cold forms a fine mealy powder. At 100°, it assumes a light yellow colour, without loss of weight; at 110°, it becomes lemon-yellow, with slight loss; and at 120°, brown-yellow, with loss of all its water of crystallization. It dissolves sparingly in water, and separates therefrom as a white crust by evaporation at ordinary temperatures, but as a lemon-yellow crust, by evaporation at temperatures above 50°. — The lemon-yellow salt decomposed by carbonate of soda yields lemon-yellow carbonate of lead, and a yellow solution of pyruvate of soda, which for the most part assumes the amorphous state.

Calculation, according to Berzelius.			Berzelius. *dried at* 100°.
PbO	112	56·00	55·78
$C^6H^3O^5$	79	39·50	
HO	9	4·50	4·48
$C^6H^3PbO^6 + Aq$	200	100·00	

¶ Calculation, according to Völckel.			Völckel. *dried at* 100°.
PbO	112	58·55	58·63
6 C	36	18·89	18·72
3 H	3	1·57	1·71
5 O	40	20·99	20·95
$C^6H^3PbO^6$	191	100·00	100·00 ¶

c. Acid salt. — A solution of carbonate of lead in a slight excess of pyruvic acid, dries up by spontaneous evaporation to a fissured gum, which reddens litmus, and is decomposed by water with separation of the neutral salt *b*.

Ferrous Pyruvate. — *a. Crystalline.* — If a crystal of ferrous sulphate be immersed in cold water which is nearly saturated with crystalline pyruvate of soda, and the liquid covered with a layer of oil to keep out the air, it immediately assumes a dark red colour, and deposits after 24 hours, a large number of light red granules of ferrous pyruvate. The mother-liquor, which has a much deeper red colour than the granules [perhaps because it contains amorphous salt], is decanted; the crystalline granules washed with a small quantity of cold water; the liquid pressed out; and the granules dried over oil of vitriol. The salt is of a beautiful flesh colour; tastes like other ferrous salts; is permanent in the air when dry; dissolves sparingly in water, forming a yellowish solution; and is precipitated with greyish blue colour by ammonia.

β. Amorphous. — Iron is dissolved in warm dilute pyruvic acid covered with a layer of oil, the solution taking place slowly, till no more hydrogen gas is evolved; and the thick, opaque, dark red liquid evaporated by heat, whereby a nearly black, soft mass is obtained, which hardens in cooling and dissolves with deep red colour in water and in alcohol. The solution, when evaporated in the air, assumes a lighter colour, and deposits basic ferric pyruvate, a neutral salt remaining in solution.

Ferric Pyruvate. — a. *Basic.* — Precipitated from the aqueous solution of the ferrous salt on exposure to the air. Resembles hydrated ferric oxide, but dissolves with dark red colour in ammonia.

b. Neutral. — The acid saturated with recently precipitated hydrated ferric oxide, leaves, on evaporation, a red mass which dissolves in water and alcohol with the colour of other ferric salts. The solution is not precipitated by ammonia, or by caustic potash and soda or their carbonates. If the mixture of the solution with ammonia be left to evaporate spontaneously, all the ammonia is given off, and the remaining viscid syrup forms a clear solution in water. — If, however, the neutral ferric salt has been obtained by evaporating the solution of the amorphous ferrous salt in contact with the air, it forms with caustic potash and carbonate of potash, a brown precipitate somewhat soluble in excess of the reagent.

Pyruvate of Cobalt. — *a. Crystalline.* — When fragments of carbonate of cobalt are gradually introduced into the aqueous acid, the salt *a* is precipitated, in proportion as the red solution becomes saturated, in the form of a rose-coloured, granular powder, which dissolves very slowly in cold water, even when it is mixed with pyruvic acid. — *β. Amorphous.* — When the salt *a* is dissolved in warm water, or carbonate of cobalt in the boiling acid, the pale red solution yields, on evaporation, a fissured, rose-coloured gum, which does not dissolve in caustic potash or in carbonate of potash.

Pyruvate of Nickel. — Behaves just like the cobalt-salt in the states *a* and *β*, excepting that it is of an apple-green colour, and dissolves in water still more slowly.

Pyruvate of Copper. — *a. Neutral.* — *α. Crystalline.* — 1. The aqueous acid dissolves carbonate of copper with brisk effervescence, and as the saturation proceeds, deposits the salt *a*, *a* as a sea-green powder, while the salt *b* remains in solution. — 2. When a tolerably large crystal of sulphate of copper is immersed in aqueous pyruvate of soda, the solution gradually thickens from formation of a fine white precipitate of the same salt. The salt is washed with cold water and dried at ordinary temperatures. After drying in the air, it is almost pure white; when more completely dried over oil of vitriol, it turns bluish, and finally, after the loss of all the hygroscopic water, light blue. It then still retains 1 At. water. It dissolves very sparingly in cold water, forming a very pale green solution, which, when evaporated at ordinary temperatures, leaves the salt in the form of a white powder. In boiling water, it dissolves somewhat more abundantly, with a more decided green colour.

	Dried over oil of vitriol.			Berzelius.
CuO	40	....	31·25	..... 30·81
$C^6H^3O^5$	79	....	61·72	
HO	9	....	7·03	
$C^6H^3CuO^6 + Aq$	128	....	100·00	

β. Amorphous. — The solution of *a* in hot water, leaves when evaporated over the water-bath, a clear, green, fissured gum which dissolves in water with tolerable facility. Its solution in caustic ammonia or carbonate of ammonia evaporated in the open air, leaves a dark green fissured mass; the solution in potash-ley is dark blue, becomes turbid and assumes a green colour when diluted, and deposits a black-brown oxide when boiled.

b. *Acid salt.* — The above-mentioned mother-liquor, from which the crystalline neutral salt prepared by (1) has been deposited. It dries up to a transparent green gum, which is decomposed by water.

Mercurous Pyruvate. — The aqueous solution of the crystalline soda-salt forms a white magma with mercurous nitrate. This salt dissolves in boiling water, the undissolved portion turning grey—and separates on cooling in the amorphous state. — If the amorphous soda-salt be used, the same precipitate is obtained, but it then decomposes still more readily, the decomposition taking place after a while, even in the cold.

Mercuric Pyruvate — *a. Basic.* — Separates on treating the salt *b* with water. White, tumefied, insoluble in water. — *b. Neutral.* — 1. When the dilute acid is saturated with finely pulverized mercuric oxide, filtered after some hours, and the colourless filtrate, which tastes like corrosive sublimate, left to evaporate, the neutral salt separates out in the form of a white crust, while the salt *c* remains in the mother-liquid. — 2. An aqueous solution of equal numbers of atoms of corrosive sublimate and pyruvate of soda, likewise deposits a white crust by spontaneous evaporation. The salt *b* is decomposed by water, which leaves the basic salt *a* undissolved. — *c. Acid salt.* — The mother-liquor of the salt *b* prepared by (1) dries up to a transparent gum, which is decomposed by water into the basic salt *a* and a solution of a hyperacid salt. This solution forms with ammonia a precipitate which does not redissolve in a larger quantity of ammonia; but the precipitate produced by alkaline carbonates dissolves in excess of the reagent, forming a liquid from which

a grey mercurous salt separates; this liquid also yields a white mercurous salt by spontaneous evaporation.

Pyruvate of Silver. — *a. Crystalline.* — 1. The cold dilute acid is saturated with excess of recently precipitated oxide of silver (not with carbonate, which forms a greyish yellow salt, with reduction of a large quantity of silver). The liquid, which thickens by separation of laminæ, is diluted with boiling water till the laminæ dissolve; filtered boiling; and the filtrate left to cool slowly in a dark place till it crystallizes. — 2. A mixture of the aqueous soda-salt with nitrate of silver forms after a while the same crystals, which must be pressed after pouring off the liquid, dissolved in boiling water, left to crystallize therefrom, and dried in the dark over oil of vitriol. — Large, shining, milk-white scales, resembling boracic acid, greasy to the touch, and turning brown by exposure to the sun. The crystals are free from water of crystallization, and after drying at ordinary temperatures, suffer no loss of weight when left over oil of vitriol at 100°. By dry distillation, they yield pyruvic acid, smelling strongly of acetic acid, and a grey metallic-looking residue of carbide of silver (VI, 146). The salt when heated in the air, takes fire at the hottest point, and continues to glow spontaneously, till nothing is left but 55·26 per cent of silver, in the form of scales. The salt dissolves very sparingly in cold water; its solution in hot water deposits by warm evaporation a brown powder, but remains colourless, and on cooling yields more crystals of the pure salt; but if heated for a longer time, it turns yellow and yields, on cooling, yellow crystals of an altered salt. The yellow solution heated to the boiling point gives off carbonic acid, and deposits carbide of silver as a grey metallic powder. The salt dissolves in aqueous ammonia, and when treated with carbonate of potash, yields carbonate of silver insoluble in excess.

β. Amorphous. — The amorphous soda-salt forms with nitrate of silver a white flocculent precipitate which dissolves in hot water somewhat more readily than in cold, and is deposited in the amorphous state on cooling. The solution, when heated, assumes a lighter colour than that of the salt *a*, and deposits carbide of silver.

	Crystals a.			Berzelius.
6 C	36	....	18·46	18·36
3 H	3	....	1·54	1·83
Ag	108	....	55·38	55·26
6 O	48	....	24·62	24·55
$C^6H^3AgO^2,O^4$	195	....	100·00	100·00

Pyruvic acid mixes in all proportions with *Alcohol* and *Ether* (Berzelius).

β. Oxygen-nucleus. $C^6H^2O^4$

Mesoxalic Acid. $C^6H^2O^{10}=C^6H^2O^4,O^6$.

Liebig & Wöhler (1838). *Ann. Pharm.* 26, 298.
Svanberg. *Berzelius, Jahresber.* 27, 165.

Produced by boiling alloxan or alloxanic acid with the stronger bases and water.

Mesoxalate of baryta is decomposed with an equivalent quantity of dilute sulphuric acid; or the lead-salt suspended in water is decomposed by sulphuretted hydrogen, the liquid filtered, and the filtrate evaporated to the crystallizing point (Liebig & Wöhler).

The acid is crystallizable and very sour (Liebig & Wöhler).

	Calculation.		
6 C	36	.....	30·51
2 H	2	.....	1·69
10 O	80	.....	67·80
$C^6H^2O^4,O^6$	118	.....	100·00

Dissolves readily in water.

Mesoxalate of Baryta. — When a hot-saturated solution of alloxanate of baryta is boiled, a mixture of alloxanate, mesoxalate and carbonate of baryta is precipitated; and the filtrate, when further evaporated, yields pure mesoxalate of baryta in yellow laminæ, which must be washed with alcohol to free them from adhering urea. The acid precipitates baryta, strontia, and lime salts, only on addition of ammonia (Liebig & Wöhler). — At 90°, the salt is anhydrous $=BaO,C^3O^4$, $[=C^6Ba^2O^4,O^6]$; it begins to decompose at 100°, but a higher temperature is required to decompose it completely (Svanberg).

	Crystallized.			Liebig & Wöhler.
2 BaO	153·2	....	56·49	..... 55·93
6 C	36·0	....	13·27	
2 H	2·0	....	0·74	
10 O	80·0	....	29·50	
$C^6Ba^2O^{10}+2Aq$	271·2	....	100·00	

Mesoxalate of Lime. — Thin tables, which, after drying at 90°, $=C^6Ca^2O^{10}+4Aq.$; give off 2 Aq. more at 140°; decompose and bake into lumps above 140°. Much more soluble in water than the baryta salt (Svanberg).

Mesoxalate of Lead. — *a. Basic.* — When a solution of alloxanic acid or alloxan is dropt into a boiling solution of neutral acetate of lead, a white bulky precipitate is formed, which on boiling aggregates into a fine, heavy, crystalline powder. — The decomposition induced by heating the salt at a particular point, spreads from thence through the entire mass, and after gentle ignition in contact with the air, pure protoxide of lead remains behind. A small quantity of ammonia is evolved in the decomposition, because the lead-salt, at the moment of its formation, carries down with it a trace of nitrogenous matter, probably cyanate of lead, the quantity being greater as the liquid has been less boiled. Hot nitric acid converts the salt into oxalate of lead (Liebig & Wöhler).

				Liebig & Wöhler.
4 PbO	448	....	81·75	..... 80·78
6 C	36	....	6·57	..... 6·89
8 O	64	....	11·68	..... 12·14
H		....		..... 0·19
$2PbO+C^6Pb^2O^{10}$	548	....	100·00	..... 100 00

b. Neutral. — Mesoxalic acid forms with neutral acetate of lead a

precipitate, in which half the lead-oxide is replaced by water (Liebig & Wöhler). [Probably therefore $C^6Pb^2O^{10} + 2$ Aq.].

Mesoxalate of Silver. — Mesoxalic acid forms with nitrate of silver, on addition of ammonia, a yellow precipitate, which, when gently heated, is completely resolved, with violent effervescence, into carbonic acid and metallic silver; hence its composition must be analogous to that of the first mentioned lead-salt (Liebig & Wöhler):

$$C^6Ag^4O^{12} = 6CO^2 + 4Ag.$$

Iodine-nucleus. C^6H^5I.

¶ Iodopropylene. C^6H^5I.

Berthelot and De Luca. *Compt. rend.* 39, 745.

Formation, p. 395.

Preparation. Biniodide of phosphorus is prepared by Corenwinder's method, viz. by dissolving 25 grm. phosphorus and 200 grm. iodine in bisulphide of carbon, and evaporating the solvent in a current of dry carbonic acid. 100 grm. of this iodide (PI^2), are then mixed in a tubulated retort with 50 grm. of syrupy glycerine (commercial glycerine purified and evaporated till it boils at 160°); and the action aided at the commencement by a gentle heat: about 30 grm. of iodurетted propylene then condense in the receiver, which must be kept cool. The product is purified by distillation, the portion which passes over at 101° being collected apart.

Properties. Liquid, of sp. gr. 1·789 at 160°. Colourless when first prepared, but rapidly becomes coloured by the action of air and light; after this change, it gives off very irritating vapours. The odour of the recently prepared compound is ethereal when first inhaled, then alliaceous.

Calculation.

6 C	36	21·56
5 H	5	2·99
I	126	75·45
C^6H^5I	167	100·00

Isomeric with iodide of mesityl (p. 26).

Decompositions. 1. By the action of zinc or mercury with hydrochloric or dilute sulphuric acid, iodopropylene is converted into propylene (vid. p. 396). — 2. Strong sulphuric acid has no action upon it in the cold, but carbonizes it at high temperatures, evolving a small quantity of propylene. — 3. Fuming nitric acid decomposes it instantly, with precipitation of iodine. — 4. Aqueous ammonia acting for 40 hours on iodo-propylene at a temperature of 100°, decomposes it completely, with formation of a volatile alkali, which appears to be propylamine [?], (Berthelot & De Luca).

Combinations. Iodopropylene is insoluble in water, but dissolves in *alcohol* and in *ether* (Berthelot & De Luca). ¶

[illegible] Bromine-nucleus.

[illegible] Bromine-nucleus. [illegible]

Bromopropionic Acid. [illegible]

[illegible] (1847). *J. Ann. Chim. Phys.* [illegible]; also *J. pr. Chem.* [illegible]

Bromometacetone acid. Bromoacetobutyric acid. Acide bromitonique.

Bromine is gradually added in excess to a concentrated aqueous solution of [illegible] of potash containing an excess of potash; the oil which sinks down with abundant evolution of carbonic acid, treated with aqueous potash, which takes up the bromopropionic acid and leaves a small quantity of a neutral oil [illegible]; the acid precipitated from the potash-solution by the addition of a stronger acid; and the white crystalline [illegible] washed with the smallest possible quantity of cold water, pressed between paper, dried in vacuo, dissolved in ether, and the ethereal solution [illegible] crystallizes.

Long snow-white silky needles, which, when carefully heated, volatilize almost completely without decomposition.

						Cahours.
[illegible]	[illegible]	—	[illegible]	—		[illegible]
[illegible]	[illegible]	—	[illegible]	—		[illegible]
[illegible]	[illegible]	—	[illegible]	—		[illegible]
[illegible]	[illegible]	—	[illegible]	—		[illegible]
[illegible]	[illegible]	—	[illegible]	—		[illegible]

With oil of vitriol, this acid behaves in the same manner as bromobutyric acid, [illegible].

It dissolves with tolerable facility in *Water*, especially at the boiling heat; and crystallizes out as the liquid cools.

It dissolves in all proportions in *Alcohol* and *Ether* (Cahours).

β. *Bromine-nucleus.* $C^6Br^3H^3$.

Terbromopropylic Aldide. $C^6Br^3H^3,O^2$.

CAHOURS. (1847). *N. Ann. Chim. Phys.* 19, 504; also *J. pr. Chem.* 41, 76.

Tribromoxaldid [*Nesixim*].

Bromine is gradually added to a concentrated aqueous solution of neutral itaconate or citraconate of potash, till no more carbonic acid is given off; and the precipitated oil freed from adhering bromobutyric acid by agitation with dilute potash, then washed with water, and dried in vacuo. The product is but small.

Amber-coloured, tolerably fluid oil, heavier than water, and having an agreeable aromatic taste.

			Cahours.
6 C	36	12·21	11·64
3 H	3	1·02	1·15
3 Br	240	81·35	83·23
2 O	16	5·42	3·98
$C^6Br^3H^3O^2$	295	100·00	100·00

May be regarded as acetone in which 3H are replaced by 3Br.

The oil is partially decomposed by heat, giving off hydrobromic acid, and leaving charcoal.

It is perfectly insoluble in water and in aqueous alkalis.

It mixes in all proportions with alcohol and ether (Cahours).

If the itaconate or citraconate of potash contains excess of potash, this process yields another heavy oil richer in carbon (Cahours).

c. Chlorine-nucleus. $C^6Cl^3H^3$.

Chlorosuccic Acid. $C^6Cl^3H^3,O^4$.

MALAGUTI. (1846). *N. Ann. Chim. Phys.* 16, 67, 72 and 82.

Acide chlorosuccique (Malaguti); *Acide metacétique bichloré* (Gerhardt).

Formation. From a solution of perchlorosuccinic ether in warm alcohol, water throws down an oily mixture of perchlorocarbonic ether, terchloracetic ether, and chlorosuccic ether. — 2. Perchlorosuccinic ether decomposed by aqueous potash yields chlorosuccate of potash, in addition to chloride of potassium, carbonate of potash, and formiate of potash. — Vid. *Perchlorosuccinic ether.*

Preparation. Perchlorosuccinic ether is dissolved in hot alcohol; a few pieces of hydrate of potash added to the precipitated oily mixture of the three ethers, whereupon the alcohol volatilizes and the mass becomes heated to the boiling point; and the mass stirred, with addition of water, to prevent the heat from rising high enough to blacken it. The mass is then dissolved in water: the solution supersaturated with hydrochloric acid, and partially evaporated; the chlorosuccic acid, which falls down as a yellow oil, dissolved in water and again evaporated, whereby it is again thrown down in the form of an oil; the oil redissolved in water, again evaporated, &c., till the water which stands above the oil, no longer forms a precipitate with solution of silver. The oil is then dried in vacuo over oil of vitriol and hydrate of potash, till it crystallizes after a few days, with separation of a little chloride of calcium. This crystalline mass is dissolved in absolute alcohol; the solution quickly decanted from the chloride of calcium, and evaporated in vacuo; the crystalline residue freed by repeated pressure from an unctuous substance formed by decomposition of the alcohol; and this solution in alcohol, evaporation, and pressing, repeated till the acid no longer leaves chloride of calcium when burnt. The purification is attended with great loss, which is even increased by using ether instead of alcohol.

Properties. Colourless; crystalline; melts at 60°, and crystallizes on cooling in a mass having a silky lustre; at 75°, it diffuses itself in

white clouds which condense on cold bodies in silky needles. Has an extremely sour taste, and forms white spots upon the tongue. Permanent in the air.

Calculation, acc. to Gerhardt.			Calculation, acc. to Malaguti.			Malaguti.
6 C	36·0	20·32	6 C	36·0	21·40	21·52
3 Cl	106·2	59·93	3 Cl	106·2	63·14	63·07
3 H	3·0	1·69	2 H	2·0	1·19	1·25
4 O	32·0	18·06	3 O	24·0	14·27	14·16
$C^6Cl^3H^3O^4$	177·2	100·00	$C^6Cl^3H^2O^3$	168·2	100·00	100·00

Malaguti fused the acid before analyzing it. Gerhardt suggests (*N. J. Pharm.* 14, 235) that it was hereby partially converted into *chlorosuccid*, $C^6Cl^3HO^3$, and consequently the analysis gave too little H and O.

The *Ammonia-salt* crystallizes in long asbestus-like fibres.

The dilute acid does not precipitate any heavy metallic salts.

The concentrated acid forms with *nitrate of silver* a crystalline magma, consisting of delicate shining needles, which are but little affected by light at ordinary temperatures, but are very susceptible of its influence when heated (Malaguti).

Calculation, acc. to Gerhardt.			Calculation, acc. to Malaguti.			Malaguti. *dried in vacuo.*
6 C	36·0	12·67	6 C	36·0	13·08	12·60
3 Cl	106·2	37·37	3 Cl	106·2	38·59	
2 H	2·0	0·70	H	1·0	0·36	0·56
Ag	108·0	38·00	Ag	108·0	39·25	39·09
4 O	32·0	11·26	3 O	24·0	8·72	
$C^6Cl^3H^2Ag_2O^4$	284·2	100·00	$C^6Cl^3HAgO^3$	275·2	100·00	

d. Nitro-nucleus. C^6XH^5.

Nitropropionic Acid. $C^6NH^5O^8 = C^6XH^5,O^4$.

Chancel. *N. Ann. Chim. Phys.* 12, 146; also *Compt. rend.* 18, 1023; also *J. pr. Chem.* 33, 453; abstr. *Ann. Pharm.* 52, 295. — *N. J. Pharm.* 7, 355. — *Compt. rend.* 21, 908.

Laurent & Chancel. *Compt. rend.* 25, 883; also *N. J. Pharm.* 13, 462.

Nitrometacetonic acid, Nitrometacetsäure, Acide metacetonitrique (formerly, *Acide butyronitrique*). — Discovered by Chancel in 1844, but at first mistaken for nitrobutyric acid.

Formation. By the action of nitric acid on metacetone or butyral ($C^6H^6O^2$) or butyrone ($C^{14}H^{14}O^2$).

Preparation. Butyrone is gently heated in a retort with a moderate quantity of strong nitric acid, till carbonic acid and nitrous fumes are abundantly evolved; then removed quickly from the fire, to prevent projection of the liquid by the violent evolution of gas which takes place; and the red vapour spassed through water, which thereby becomes covered with a layer of oil. When the evolution of gas is terminated,

the distillate is repeatedly agitated with a large quantity of water. — Another method is to boil 10 or 15 grammes of butyrone in a tubulated retort; gradually add an equal weight of boiling nitric acid; and then remove the fire.

Properties. Yellow oil, which does not solidify in a mixture of ether and solid carbonic acid; heavier than water; has an aromatic odour and a very sweet taste (Chancel).

Calculation, according to Laurent & Chancel.			
6 C	36		30·25
N	14		11·77
5 H	5		4·20
8 O	64		53·78
C^6XH^5,O^4	119		100·00

Decompositions. The acid is easily set on fire, and burns with a reddish flame (Chancel).

Combinations. The acid is insoluble in water.

The *Nitropropionates* are yellow, crystallizable, and when gently heated, detonate slightly with emission of light. Mineral acids added to their aqueous solutions, throw down the nitropropionic acid in the form of an oil (Chancel).

Nitropropionate of Ammonia. $C^6XH^4Am,O^4 + 2$ Aq. — Crystalline. May be sublimed without detonation. After remaining for some days in a stoppered bottle, it decomposes spontaneously, and is converted into a liquid which assumes the gaseous form even at ordinary temperatures. Its aqueous solution is readily decomposed by sulphuretted hydrogen, with deposition of sulphur (Laurent & Chancel).

Nitropropionate of Potash. $C^6XH^4K,O^4 + 2$ Aq. The alcoholic solution of the acid mixed with alcoholic potash, becomes heated and forms a yellowish mixture, which, after a while, deposits a great number of scales, and finally solidifies in a crystalline mass. The crystals washed with alcohol and purified by recrystallization, form yellow laminæ isomorphous with those of the ammoniacal salt (Chancel). They give off their water of crystallization (10 p.c.) at 140°, and detonate at a temperature 2° or 3° higher (Laurent & Chancel). They dissolve in 20 pts. of water, scarcely at all in alcohol (Chancel).

The aqueous solution of the potash-salt forms a yellow precipitate with *lead-salts*, and a dingy green precipitate with *copper-salts* (Chancel).

Nitropropionate of Silver. — a. *Bibasic.* $AgO,C^6XH^4Ag.O^4 + Aq.$ — The potash-salt forms with nitrate of silver a yellow precipitate which soon turns violet. It dissolves in a large quantity of water, and crystallizes out on evaporation. But when the salt is boiled with water, half the oxide of silver separates out and the monobasic salt remains dissolved. (Chancel).

b. *Monobasic.* $C^6XH^4AgO^4 + 2Aq.$ — The aqueous solution of *a* boiled and filtered from oxide of silver, yields rhombic tables by evaporation (Chancel).

Nitropropionic acid mixes in all proportions with *Alcohol.* (Chancel).

e. *Amidogen-nuclei.*

a. Amidogen-nucleus. C^6AdH^5.

Propionamide or Metacetamide. $C^6NH^7O^2 = C^6AdH^5,O^2$.

Produced immediately on bringing propionic ether (p. 409) in contact with aqueous ammonia:

$$C^{10}H^{10}O^4 + NH^3 = C^6NH^7O^2 + C^4H^6O^2.$$

It is decomposed when heated with potassium, yielding cyanide of potassium, hydrogen, and a carburetted hydrogen gas. Distilled with anhydrous phosphoric acid, it yields *Metacetonitrile*, which is identical with cyanide of ethyl (VIII, 486).

$$C^6NH^7O^2 = C^6NH^5 + 2HO.$$

(Dumas, Malaguti & Leblanc, *Compt. rend.* 25, 657).

Sarcosine. $C^6NH^7O^4 = C^6AdH^5,O^4$.

Liebig. *Ann. Pharm.* 62, 310.

Sarkosin. From σαρξ, flesh.

Preparation. 10 pts. of baryta-crystals (free from potash, soda, lime, chlorine, and nitric acid, which substances are difficult to separate from sarcosine) are added to a boiling saturated solution of 1 pt. of creatine in water; the mixture kept boiling, and the water and baryta renewed, as long as ammonia continues to escape and a precipitate of carbonate of baryta to form; the liquid filtered from this precipitate; the caustic baryta precipitated by a stream of carbonic acid gas; and the filtrate evaporated to a syrup: this syrup, when set aside, solidifies in a heap of transparent and colourless crystalline laminæ. To purify this product, the mass is dissolved in excess of dilute sulphuric acid; the solution evaporated to a syrup over the water-bath; the syrup mixed with alcohol by stirring the two together with a glass rod, till the mixture is converted into a white crystalline powder of sulphate of sarcosine; the powder washed with cold alcohol (which dissolves out a substance resembling urethane); dissolved in water; heated with carbonate of baryta till the liquid becomes neutral; and the filtrate evaporated over the water-bath to a syrup, which crystallizes in 24 to 36 hours.

Properties. Transparent, colourless, right-rhombic prisms, acuminated with two faces resting on the obtuse lateral edges (*Fig.* 65). $u' : u = 77°$. They retain their appearance unaltered at 100°; melt at a somewhat higher temperature; and when heated to 100° between two watch-glasses, sublime in the form of a crystalline network. The aqueous solution has a sweetish, sharp, and somewhat metallic taste, and is neutral to vegetable colours.

	Crystals.			Liebig.
6 C	36	....	40·45	40·73
N	14	....	15·73	15·84
7 H	7	....	7·86	7·90
4 O	32	....	35·96	35·53
$C^6NH^7O^4$	89	....	100·00	100·00

Sarcosine is in the propylene-series what glycocol (p. 247) is in the ethylene-series (Laurent & Gerhardt, *N. J. Pharm.* 14, 314). — Liebig places sarcosine among the alkaloids.

Combinations. Sarcosine dissolves with great facility in water.

Sulphate of Sarcosine. — *Preparation* (p. 432). The salt, after washing in cold alcohol, dissolves in 10 to 12 parts of boiling alcohol, and yields on cooling, transparent, colourless, highly lustrous four-sided tables resembling chlorate of potash; their solution reddens litmus. They give off 6·8 p.c. (1 At.) water at 100°. They dissolve very readily in water; crystallize from the solution in large plumose laminæ; and are very sparingly soluble in cold alcohol.

	Dried at 100°.			Liebig.
$C^6NH^7O^4,HO$	98	....	71·02	
SO^3	40	....	28·98	29·80
$C^6NH^7O^4,SO^3,HO$	138	....	100·00	

Hydrochlorate. — Sarcosine evaporated with hydrochloric acid, yields a white mass which crystallizes from alcohol in small transparent needles.

Mercury-compound. — An aqueous solution of sarcosine forms no precipitate in a dilute solution of corrosive sublimate; in a cold-saturated solution of that salt, crystallized sarcosine dissolves readily, and soon forms numerous delicate needles of the double-salt, which ultimately convert the liquid into a solid mass.

Platinum-compound. — A clear mixture of hydrochlorate of sarcosine and excess of bichloride of platinum, yields by spontaneous evaporation, large, honey-yellow, octohedral segments, which may be freed from excess of bichloride of platinum by washing with ether and alcohol. They give off 6·7 p.c. (2 At.) water at 100°, leaving a residue of $C^6NH^7O^4,HCl + PtCl^2$.

The dark blue solution of sarcosine in aqueous *cupric acetate* likewise yields, by evaporation at a gentle heat, coloured laminæ of a double salt.

Sarcosine dissolves sparingly in alcohol, and is insoluble in ether (Liebig).

¶ Alanine. $C^3NH^7O^4 = C^6AdH^5,O^4$.

A. Strecker. *Ann. Pharm.* 75, 29; *Chem. Gaz.* 1850, 409; *Jahresber.* 1850, 382.

Formation. By the action of hydrocyanic acid on aldehyde-ammonia in presence of dilute hydrochloric acid, and with the aid of heat:

$$C^4H^4O^2,NH^3 + C^2NH + HCl + 2HO = C^6NH^7O^4 + NH^4Cl.$$

If the mixture of aldehyde-ammonia, hydrocyanic acid, and dilute hydrochloric acid (the latter being in sufficient quantity to produce a slight acid reaction) be left to itself in a close vessel at ordinary temperatures, a different action takes place, the liquid after a while depositing crystals of *Hydrocyanaldine*, $C^{18}N^4H^{12}$:

$$3(C^4H^4O^2,NH^3) + 3C^2NH + 2HCl = C^{18}N^4H^{12} + 6HO + 2NH^4Cl.$$

When the aldehyde-ammonia and hydrocyanic acid are heated together without admixture of hydrochloric acid, a totally different action takes place, hydrocyanate of ammonia going off, the mass acquiring a deep brown colour, and a substance being formed which crystallizes in thin colourless needles, and dissolves very readily in ether.

Preparation. An aqueous solution of aldehyde-ammonia is mixed with hydrocyanic acid, in the proportion of 2 pts. by weight of aldehyde-ammonia to 1 pt. anhydrous hydrocyanic acid, aqueous hydrochloric acid added in excess, and the mixture distilled in a retort. Hydrochloric acid then passes over, together with a small quantity of hydrocyanic acid, and if the hydrochloric acid was very concentrated, a small quantity of formic acid; and after the liquid in the retort has been evaporated to half its bulk, which is best effected at the heat of the water-bath, a large quantity of sal-ammoniac crystallizes out, and there remains a thick strongly acid mother-liquor containing hydrochlorate of alanine. To separate this compound from the sal-ammoniac, the mass, after being freed as completely as possible from excess of hydrochloric acid by continued heating to 100°, is mixed with a small quantity of water; the liquid filtered from the undissolved chloride of ammonium; the latter washed with a small quantity of cold water; the filtrate freed from hydrochloric acid and chloride of ammonium by boiling with hydrated oxide of lead, which must be added as long as ammonia continues to escape; the filtrate freed from lead by sulphuretted hydrogen; and the liquid, after filtration from the sulphide of lead, evaporated to the crystallizing point. The alanine then separates out; a little more may be precipitated from the mother-liquor by addition of alcohol. The crystals are purified from hydrochloric acid by washing with alcohol. — The mixture of hydrochlorate of alanine and chloride of ammonium first obtained, may also be mixed with alcohol and a small quantity of ether, in which the hydrochlorate of alanine dissolves readily, the sal-ammoniac but sparingly. The alcohol and ether are then evaporated, and the solution freed from hydrochloric acid and a small quantity of ammonia, by means of hydrated oxide of lead.

Properties. Crystallizes on cooling from hot saturated solutions, in colourless needles, having the form of oblique rhombic prisms, and united in tufts: the aqueous solution, when evaporated, yields a crust, and below

it a number of capillary crystals. The larger crystals have a pearly lustre, are hard, and grate between the teeth. At 200° it sublimes, and falls down again in fine snowy crystals; when suddenly heated, it fuses with partial decomposition. When rapidly heated on platinum foil, it burns away with a violet flame.

	Dried at 100°.		Strecker (*mean*).
6 C	36	40·45	40·35
N	14	15·73	15·32
7 H	7	7·86	7·81
4 O	32	35·96	
$C^6NH^7O^4$	89	100·00	

Isomeric with urethane, lactamide, and sarcosine; from the two former it is distinguished by not melting below 100°; from the last, by being less soluble in water, less volatile, and by forming compounds with metallic oxides.

Decompositions. — Alanine is not altered by boiling with acids; it dissolves in strong sulphuric acid, and the solution does not blacken or give off sulphurous acid, even at a boiling heat. — 1. Alanine is decomposed by nitrous acid, with evolution of nitrogen and formation of lactic acid:

$$C^6NH^7O^4 + NO^3 = C^6H^6O^6 + 2N + HO.$$

2. Alanine is not altered by boiling with solution of potash; but if the mixture be concentrated by evaporation till the potash is nearly reduced to the solid hydrate, ammonia is evolved, together with a considerable quantity of hydrogen; and if the operation be then interrupted, and the residue distilled with dilute sulphuric acid, hydrocyanic acid and water pass over, together with a volatile acid, which has a powerful acid reaction, and appears to be acetic acid. — 3. Alanine heated in the state of aqueous solution with peroxide of lead, is decomposed, with formation of carbonic acid, aldehyde, and ammonia. The same products are formed on boiling it with peroxide of lead and dilute sulphuric acid; the distillate has then a strong acid reaction, due probably to acetic acid formed from the aldehyde by oxidation. The distillate does not appear to contain any nitrogenous body.

Combinations. 1. Alanine dissolves in 4·6 pts. of *Water* at 17°, and in a smaller quantity of hot water. The solution has a sweet taste, does not affect vegetable colours, and forms no precipitates with any of the ordinary reagents.

2. With *Acids.* — Alanine dissolves in dilute acids more readily than in water, without however neutralizing their action on vegetable colours; it is not separated from the solution by addition of alcohol. When a solution of alanine in an easily volatile acid is evaporated, there remains a strongly acid mass, consisting of a compound of alanine with the acid. The compounds of alanine with acids all dissolve in alcohol more readily than alanine itself, and likewise dissolve for the most part in a mixture of alcohol and ether.

Sulphate of Alanine. — Very soluble in water. Remains when the solution is evaporated, in the form of a syrupy mass, which solidifies in crystals after some time only. It may be freed from excess of sulphuric acid by washing with a small quantity of alcohol. Absolute alcohol does not precipitate he salt, even from its most concentrated aqueous

solution; but a mixture of alcohol and ether separates it in the form of a thick syrup.

Hydrochlorate of Alanine. *a.* $2C^6NH^7O^4,HCl$. — Obtained by passing dry hydrochloric acid gas over dry alanine, or by dissolving 2 At. alanine in 1 At. hydrochloric acid. 100 pts. alanine take up 20·3 p.c. hydrochloric acid; the above formula requires 20·5 p.c. — The solution, when evaporated or mixed with alcohol, yields the compound in colourless crystals. Dissolves readily in water, sparingly in alcohol.

				Strecker.
$2\,C^6NH^7O^4$	178·0	83		
HCl	36·4	17		20·5
$2C^6NH^7O^4,HCl$	214·4	100		

The salt analyzed was prepared by dissolving alanine in less than an equivalent quantity of acid, and was contaminated with the following compound *b*.

b. $C^6NH^7O^4,HCl$. — Obtained, though not easily in a state of purity, by evaporating a solution of alanine in excess of hydrochloric acid. Extremely deliquescent and very soluble in alcohol.

	Dried at 100°.		Strecker.
$C^6NH^7O^4$	89·0	70·9	
HCl	36·4	29·1	30·2
$C^6NH^7O^4,HCl$	125·4	100·0	

Nitrate of Alanine. — Remains in the form of long colourless needles when a solution of alanine in dilute nitric acid is slowly evaporated. The crystals deliquesce in damp air, and dissolve very readily in water, somewhat less freely in alcohol. After drying over oil of vitrol, they do not at first diminish in weight at 100°; but nevertheless they gradually undergo an alteration, indicated by the assumption of a yellow colour.

			Strecker.
6 C	36	23 68	23·90
8 H	8	5·26	5·47
2 N	28	18·42	
10 O	80	52·64	
$C^6NH^7O^4,NO^6H$	152	100·00	

Platinum-salt. — Neither the aqueous nor the alcoholic solution of hydrochlorate of alanine forms any precipitate with bichloride of platinum. But on evaporating a mixture of the two salts, treating the nearly dry mass with a mixture of alcohol and a small quantity of ether, and leaving the resulting solution to evaporate, the chloroplatinate of alanine separates in delicate yellow needles, which are soluble in water, alcohol, and ether. At 100°, the crystals assume a dark colour, and diminish continually in weight; and when dissolved in water, after exposure to this temperature for some time, leave a residue of chloroplatinate of ammonium.

	Dried at the ordinary temperature.		Strecker.
12 C	72	13·0	
2 N	28	5·0	
15 H	15	2·7	
2 Pt	198	35·7	35·4
5 Cl	177	32·0	
8 O	64	11·6	
$2(C^6NH^7O^4),HCl,2PtCl^2$	554	100·0	

This salt affords a marked distinction between alanine and sarcosine, the chloroplatinate of sarcosine being insoluble in a mixture of alcohol and ether, and crystallizing in large octohedrons (p. 433).

c. Alanine combines with *Metallic oxides*, forming compounds which may be regarded as alanine in which 1 At. hydrogen is replaced by 1 At. of the metal. The compounds have an alkaline reaction, in those cases in which the metallic oxide itself exhibits that reaction.

Barium-compound. — An aqueous solution of alanine boiled with carbonate of baryta takes up a large quantity of baryta, acquiring thereby an alkaline reaction. The liquid yields by evaporation a crystalline compound of alanine and baryta, which is soluble in water, and imparts to that liquid an alkaline reaction. A stream of carbonic acid gas passed through the solution, throws down nearly all the baryta in the form of carbonate; but the precipitate disappears again when boiled for some time with the solution.

Lead-compound. $2C^6NH^6PbO^4 + PbO,HO$. — Protoxide of lead boiled with an aqueous solution of alanine is dissolved in considerable quantity, forming a solution which, when evaporated and cooled, yields vitreous colourless needles. The aqueous solution mixed with alcohol becomes turbid, and solidifies in a mass of needles arranged in radiating groups. The crystals, when dried over oil of vitriol, give off water, and crumble to a white mealy powder, which is no longer completely soluble in water. The filtered solution has an alkaline reaction, and when exposed to the air, becomes turbid and deposits carbonate of baryta. The compound prepared by boiling alanine with excess of oxide of lead, and precipitating with alcohol, gave off 8·6 p.c. water at 100°; and the dried product yielded by analysis 66·87 p.c. oxide of lead. According to the above formula, the quantity of oxide of lead in the salt dried at 100° should be 66·45 per cent; and the quantity of water given off corresponds to 5 At. (= 8·2 p.c.).

Copper-compound. — An aqueous solution of alanine acquires a dark blue colour by boiling with cupric oxide, and yields by evaporation deep blue crystals, which appear under the microscope to consist of somewhat elongated six-sided tables, but partly also of thickish rhombic prisms. The crystals undergo no change at 100°; but at a higher temperature, they assume a light blue colour without alteration of form, and afterwards yield a bluish white powder. After drying at 100°, they give off at 120°, a quantity of water amounting to 6·5 p.c. (or 1 At.). The compound dissolves pretty readily in water, forming an intensely coloured solution, which becomes almost colourless on addition of nitric acid. In alcohol it is nearly insoluble:

	Dried at 120°.		Strecker.
6 C	36·0	30·07	29·97
6 H	6·0	5·01	5·17
N	14·0	11·70	
3 O	24·0	20·05	
CuO	39·7	33·17	33·25
$C^6NH^6CuO^4$	119·7	100·00	

	Dried at 100°.			Strecker.
$C^6NH^7O^4$	89·0	....	69·15	
CuO	39·7	....	30·85	..... 30·95
$C^6NH^7O^4,CuO = C^6NH^6CuO^4,HO$	128·7	....	100·00	

Silver-compound. — Alanine boiled with silver-oxide and water, forms a colourless solution, which on cooling yields small yellowish needles, uniting in hemispherical masses. They dissolve readily in water, and the solution may be boiled without decomposition. They quickly assume a dark colour when exposed to light; and turn brown when heated for some time to 100° in the moist state. After drying at ordinary temperatures, they may be heated to 100° without alteration (Strecker).

	Dried at 100°.			
$C^6NH^6O^4$	88	....	44·9	
Ag	108	....	55·1	..... 55·2
$C^6NH^6AgO^4$	196	....	100·0	¶

Conjugated Compound.

Cystine. $C^6NH^7S^2O^4 = C^4AdH^5,2SO^3$.

Wollaston. *Phil. Trans.* 1810, 223; also *Schw.* 4, 193; also *Ann. Chim.* 76, 22.
Lassaigne. *Ann. Chim. Phys.* 23, 328; also *Schw.* 40, 280; also *N. Tr.* 9, 1, 267.
Baudrimont & Malaguti. Abstr. *J. Pharm.* 24, 633.
Thaulow. *Ann. Pharm.* 27, 197.
Marchand. *J. pr. Chem.* 16, 254.

Cystin, Cystic Oxide, Blasenoxyd. Discovered by Wollaston in 1810. — In very rare instances, the urinary calculi and gravel of men and dogs consist of this substance (Robert, *J. Pharm.* 7, 165; Buchner, *Repert.* 21, 113; Walchner, *Schw.* 47, 106; Wurzer, *Schw.* 56, 472; Schindler, *Mag. Pharm.* 29, 264; Venables, *N. Quart. J. of Sc.* 7, 30; O. Henry, *J. Pharm.* 23, 11; Dranty, *J. Chim. méd.* 13, 230; Taylor, *Phil. Mag. J.* 12, 337; Lecanu & Ségalas, *J. Pharm.* 24, 460; Schweig. *Heidelb. Medic. Annal.* 13, 364).

Purification. If the calculus contains phosphate of lime as well as cystine, the latter is either dissolved out by ammonia, and the filtrate left to evaporate to the crystallizing point; or it is dissolved in potash, and precipitated from the filtrate by acetic acid (Lassaigne).

Properties. In urinary calculi, cystine presents the appearance of a yellowish, shining, confusedly crystallized mass (Wollaston); wax-yellow, translucent, elongated square octohedrons (Schindler); yellowish, translucent, with a faint lustre; confusedly crystalline; crackles between the teeth; is easily rubbed to a yellowish powder; tasteless, neutral (Robert). Sp. gr. of a calculus containing 97·5 pts. cystine to 2·5 pts. phosphate of lime=1·577 (Wollaston); of a calculus containing 91 per cent of cystine

= 1·13 (Taylor); of a pure cystine calculus = 1·7143 (Venables). From a solution in hot aqueous potash, cystine slowly crystallizes on addition of acetic acid, in neutral, six-sided laminæ (Wollaston); from an ammoniacal solution by evaporation, in transparent, colourless laminæ (Lassaigne); in rhombic crystals (Thaulow.)

		Thaulow.	Marchand.	Prout.	Lassaigne.
6 C	36	29·75	30·01	29·88	36·2
N	14	11·57	11·00	11·88	11·85	34·0
7½H	7	5·78	5·10	5·12	12·8
2 S	32	26·45	28·38	25·55	
4 O	32	26·45	25·51	53·15	17·0
$C^6NH^7S^2O^4$	121	100·00	100·00	100·00	100·0

Prout and Lassaigne (whose analysis differs so widely from the rest as to lead to the suspicion that he must have examined another substance) overlooked the sulphur, which was first pointed out by Baudrimont & Malaguti. Thaulow supposes cystine to contain only 6 H, which certainly agrees better with his analysis, but gives an uneven number. — According to the formula, $C^6AdH^5,2SO^2$, cystine is similar in composition to urethane and taurin.

Decompositions. 1. Cystine yields by dry distillation, carbonate of ammonia, a volatile and viscid stinking oil, and spongy charcoal (Wollaston, Walchner). It likewise gives off hydrocyanic acid (Schindler). — 2. When heated in the air, it gives off a quite peculiar and extremely disagreeable odour (Wollaston), sulphurous and resembling that of oil of mustard (O. Henry). It takes fire at the same time, without melting (Wollaston); assumes a black-brown colour; and splits into fragments, which disappear without fusion or intumescence, emitting a strong smell of hydrocyanic acid and a faint empyreumatic odour (Buchner). — 3. Fused with hydrate of potash, it gives off an inflammable gas, which burns with a flame of sulphide of carbon, producing sulphurous acid (Thaulow). — 4. Its solution in excess of nitric acid leaves, when concentrated by boiling, first a white opaque substance (Lecanu & Ségalas), then a substance which becomes continually browner, and at last black, is free from oxalic acid (Wollaston), but contains sulphuric acid (Thaulow).

Combinations. Cystine is insoluble in water (Wollaston, Robert). It dissolves in the aqueous solutions of the stronger acids; and on evaporation at a gentle heat, yields crystals which are soluble in water (Wollaston). The solution is precipitated by carbonate of ammonia (Robert).

Phosphate of Cystine. — Tufts of needles (Wollaston). Lassaigne obtained no crystals from the solution.

Sulphate of Cystine. — Tufts of needles (Wollaston). A solution of cystine in dilute sulphuric acid turns brown when somewhat strongly heated (Robert). Oil of vitriol saturated with cystine yields a colourless, viscid, non-crystallizable mass, which is soluble in water, and after drying in vacuo over oil of vitriol, contains 10·4 per cent of sulphuric acid (Lassaigne).

Hydrochlorate of Cystine. — Tufts of needles which give off hydrochloric acid at 100° (Wollaston). The needles are nearly insoluble in

water (O. Henry). When strongly heated, they give off hydrochloric acid, and leave a brown, afterwards black residue (Robert). Hydrochloric acid saturated as completely as possible with cystine, still reddens litmus. The pearly needles permanent in the air which the solution yields by spontaneous evaporation, contain, after drying in the sun, 5·3 per cent of hydrochloric acid (Lassaigne).

Nitrate of Cystine. — Tufts of needles (Wollaston). The needles have a very beautiful silky lustre, are not decomposed by sunshine, and contain 3·1 p.c. of hydrochloric acid (Lassaigne).

Cystine dissolves readily in aqueous *Ammonia*, *Potash*, *Soda* and *Lime*, also in *Bicarbonate of Potash* and *Soda*, but not in bicarbonate of ammonia. All these solutions yield granular crystals by evaporation (Wollaston). — From alkaline solutions, cystine is not precipitated by sulphuric, hydrochloric, or nitric acid; but acetic, tartaric, and citric acids precipitate it in a few seconds, as a fine white powder (Wollaston, Lassaigne, Walchner, Robert).

The solution in ammonia, when left to evaporate, yields pure cystine in crystals. — The solution in potash deposits on evaporation, white crystalline grains, which are tasteless, leave a small quantity of potash when burned, are insoluble in pure water, but dissolve readily in water containing potash (Lassaigne).

Cystine dissolves readily in aqueous *Oxalic acid* (Wollaston). The solution yields by evaporation, efflorescent needles containing 22 p.c. oxalic acid (Wollaston).

Cystine is insoluble in aqueous acetic, tartaric, and citric acid; also in alcohol (Wollaston).

¶ A substance resembling cystine and xanthine, and found in small whitish grains on the mucous membrane of the digestive organs, liver, &c. of the body, two months after interment, of a person who died of inflammation of those organs, has been examined by A. Chevallier & Lassaigne (*J. Chim. méd.* [3], 7, 208; *Pharm. Centr.* 1851, 717). The authors give to this substance the name of *Cystinoïd Tubercles* or *Xanthocystine.* ¶

β. Amidogen-nucleus. $C^4Ad^2O^4$.

Oxaluric Acid. $C^4N^2H^4O^8 = C^6Ad^2O^4,O^4$.

Liebig & Wöhler (1838). *Ann. Pharm.* 26, 287.

Formation and Preparation. 1. Parabanic acid dissolved in aqueous ammonia and heated to the boiling point, is converted into oxalurate of of ammonia. Carbonate of lime dissolved in aqueous parabanic acid, yields a solution of oxalurate of lime. — 2. A solution of murexan, exposed to oxygen gas till the purple colour at first produced has disappeared, contains oxalurate of ammonia. — 4. A solution of uric acid in warm, very dilute nitric acid, mixed with ammonia and evaporated immediately after cooling, yields crystals of yellow-coloured oxalurate of ammonia, which must be purified with animal charcoal.

The oxalurate of ammonia is dissolved in a small quantity of warm

water; mixed with sulphuric, hydrochloric, or nitric acid; the liquid cooled as quickly as possible; and the pulverulent precipitate of oxaluric acid washed.

Properties. White, loosely coherent, crystalline powder, which has a sour taste and reddens litmus.

	Crystals.			Liebig & Wöhler.
6 C	36	27·27		27·46
2 N	28	21·21		21·22
4 H	4	3·03		3·09
8 O	64	48·49		48·23
$C^6N^2H^4O^8$	132	100·00		100·00

Oxaluric acid may be regarded as a *Uridic acid* allied to the amidated acids, *i. e.* as Urea + Oxalic acid − 2Aq.

$$C^2N^2H^4O^2 + C^4H^2O^8 - 2HO = C^6N^2H^4O^8.$$

(Laurent & Gerhardt, *N. Ann. Chim. Phys.* 24, 175).

Decompositions. The aqueous solution of the acid boiled till it no longer crystallizes on cooling, is converted into a solution of oxalate of urea; hence the name:

$$C^6N^2H^4O^8 + 2HO = C^4H^2O^8 + C^2N^2H^4O^2;$$

[or: $C^6Ad^2O^8 + 2HO = C^4H^2O^8 + C^2Ad^2O^2$].

Combinations. The acid dissolves very sparingly in cold water.

It neutralizes alkalis completely; and acids added to the solution, precipitate the oxaluric acid in the form of a white powder.

Oxalurate of Ammonia. — Silky needles, which sustain no loss at 120°, dissolve very sparingly in cold water, but more readily than the free acid, and easily in hot water.

	Crystals.			Liebig & Wöhler.
6 C	36	24·16		24·40
3 N	42	28·19		28·25
7 H	7	4·70		4·84
8 O	64	42·95		42·51
$NH^3,C^6N^2H^4O^8$	149	100·00		100·00

Oxalurate of Lime. — *a. Basic.* — Obtained by supersaturating the acid with lime-water, or by mixing the neutral salt, or the clear mixture of oxalurate of ammonia and dilute chloride of calcium, with ammonia. Thick gelatinous precipitate, which dissolves very sparingly in water, readily in dilute acids, even in acetic acid.

b. Neutral. — Concentrated solutions of oxalurate of ammonia and chloride of calcium, deposit this salt in shining transparent crystals, which dissolve sparingly in water.

Oxalurate of Silver. — The alkaline oxalurates precipitate nitrate of silver in thick white flakes; and on dissolving these in hot water, the salt separates on cooling in long, delicate, silky needles. The crystals contain no water of crystallization, and when heated, decompose without detonation, leaving metallic silver (Liebig & Wöhler).

	Crystals.			Liebig & Wöhler.
6 C	36	15·06		15·29
2 N	28	11·72		11·74
3 H	3	1·25		1·29
Ag	108	45·19		45·37
8 O	64	26·78		26·31
$C^6N^2H^3AgO^8$	239	100·00		100·00

Nitrogen-nuclei.

a. Nitrogen-nucleus. C^6NAdO^4.

Parabanic Acid. $C^6N^2H^2O^6 = C^6NAdO^4,O^2$?

Liebig & Wöhler (1838). *Ann. Pharm.* 26, 285.

Preparation. Uric acid is dissolved in 8 pts. of warm, moderately strong nitric acid; the solution evaporated, after the evolution of gas has ceased, and cooled: parabanic acid then separates, often very abundantly, in colourless laminæ. These are dried upon a brick, and twice crystallized from water.

Properties. Thin, transparent, colourless, six-sided prisms, having a very sour taste, like that of oxalic acid.

	Crystallized.			Liebig & Wöhler.	Laur. & Gerh. *dried at* 110°.
6 C	36	31·58		31·91	31·4
2 N	28	24·56		24·62	
2 H	2	1·75		1·93	1·8
6 O	48	42·11		41·54	
$C^6N^2H^2O^6$	114	100·00		100·00	

The parabanic acid analyzed by Laurent & Gerhardt (*N. Ann. Chim. Phys.* 24, 175) was prepared from uric acid by means of a mixture of chlorate of potash and hydrochloric acid.

Decompositions. The acid assumes a reddish colour at 100°, without efflorescing, and melts at a stronger heat, partly subliming and partly decomposing, with evolution of hydrocyanic acid. — It does not decompose when its solution in water or in aqueous acids is boiled. — It dissolves abundantly in aqueous ammonia, forming a colourless neutral solution, which when boiled and immediately cooled, deposits so large a crop of needles of oxalurate of ammonia, that it solidifies to a magma, the parabanic acid being converted into oxaluric acid by taking up 2HO:

$$C^6N^2H^2O^6 + 2HO + NH^3 = NH^3,C^6N^2H^4O^8.$$

Carbonate of lime dissolved in aqueous parabanic acid, also yields a solution of oxalurate of lime.

Combinations. Parabanic dissolves in *Water* in larger quantity than oxalic acid.

Its aqueous solution forms with *nitrate of silver* a white pulverulent precipitate, which, on careful addition of ammonia, increases considerably and becomes gelatinous. The precipitate is insoluble in boiling water, but dissolves readily in nitric acid and ammonia. Whether prepared with or without ammonia, it contains 70·34 per cent (2 At.) of oxide of silver. Hence parabanic acid is bibasic (Liebig & Wöhler).

It is contrary to all experience that a bibasic acid, such as parabanic acid is said to be in accordance with the composition of its silver-salt, should, by addition of 2HO, be converted into a monobasic acid, viz. oxaluric acid. Parabanic acid belongs to the class of *imides*, and like those bodies, does not combine with any base, excepting oxide of silver. It is related to oxaluric acid in the same manner as phthalimide ($C^{16}NH^5O^4$) to phthalamic acid ($C^{16}NH^7O^6$), or as camphorimide ($C^{20}NH^{15}O^4$) to camphoramic acid ($C^{16}NH^{17}O^6$); and it reddens litmus only because it is converted, by the alkali contained therein, into oxaluric acid (Laurent & Gerhardt, *Compt. rend.* 27, 165; *N. Ann. Chim. Phys.* 24, 175).

β. Nitrogen-nucleus. $C^6N^2H^4$.

To this head perhaps belong the following compounds, which however require further investigation.

Allituric Acid.

Schlieper (1845). *Ann. Pharm.* 56, 20.

A solution of alloxantin in water is mixed with excess of hydrochloric acid, and rapidly boiled down to a small quantity; the pulverulent mixture of allituric acid and undecomposed alloxantin treated with nitric acid to dissolve out the latter; the residue dissolved in 15 to 20 pts. of hot water; and the solution left to deposit the allituric acid by cooling.

Yellowish white, bulky powder.

	Dried at 100°.			Schlieper.
6 C	36	....	36·37	..... 36·24
2 N	28	....	28·28	..... 28·18
3 H	3	....	3·03	..... 3·38
4 O	32	....	32·32	..... 32·20
$C^6N^2H^3O^4$	99	....	100·00	..... 100·00

When allituric acid is boiled with potash-solution till it no longer gives off ammonia, and hydrochloric acid then added to the boiling liquid, a yellowish white substance is precipitated, which, when washed and dried at 100°, contains 12·64 per cent KO, 28·64 C, 18·77 N, 2·25 H, and 37·70 O; hence it is perhaps $KO,C^{18}N^9H^{15}O^{18}$. — Nitric acid neither dissolves allituric acid nor decomposes it, even when heated.

Allituric acid dissolves in *oil of vitriol*, and is precipitated from the solution by water. — Its solution in *ammonia* yields the ammonia-salt by spontaneous, evaporation, in colourless shining needles (Schlieper).

Leucoturic Acid.

Schlieper (1845). *Ann. Pharm.* 56, 1.

Formation and Preparation. 1. Aqueous alloxanic acid is boiled for a considerable time, the water being replaced as it evaporates; then rapidly boiled down to a syrup; and the syrup dissolved in cold water, which leaves the greater part of the leucoturic acid in the form of a white powder; a little more may be obtained by evaporating the filtrate and redissolving the syrup. — 2. A concentrated aqueous solution of alloxanic acid is placed in a platinum capsule (which allows the heat to be raised somewhat higher than it could be in a porcelain dish), and rapidly evaporated to the consistence of a yellowish gum, which at first froths up strongly from escape of carbonic acid, but after two or three hours heating, fuses quietly; it is then diluted with cold water, which separates the leucoturic acid (amounting to 20 or 30 per cent of the alloxanic acid) in the form of a white powder.

Snow-white, granular, crystalline powder, and large transparent grains.

	Dried at 100°.		Schlieper.
6 C	36	31·30	31·15
2 N	28	24·35	24·51
3 H	3	2·61	2·80
6 O	48	41·74	41·54
$C^6N^2HO^6$	115	100·00	100·00

[The correctness of this formula given by Schlieper is doubtful, as Gerhardt suggests (*N. J. Pharm.* 8, 213), on account of the uneven number of atoms which it contains.]

The acid dissolved in aqueous potash decomposes when set aside for some time or gently heated, giving off ammonia, and forming a large quantity of oxalic acid:

$$C^6N^2HO^6 + 3HO = C^2O^8 + 2NH^3.$$

[Is not formic acid or some other product also formed?]

Leucoturic acid is not decomposed by boiling with strong nitric acid.

The acid is insoluble in cold *Water*, but dissolves in considerable quantity, though slowly, in hot water, and crystallizes out again on cooling.

It dissolves readily in aqueous *Alkalis*, and with the aid of heat expels carbonic acid from combination with ammonia, potash, or soda. — The solution of the acid in ammonia, which may be heated without decomposing, yields by evaporation, delicate needles of the ammonia-salt, which, when burned with oxide of copper, yields 2 vol. carbonic acid to 1 vol. nitrogen, and therefore contains 1 At. ammonia to 1 At. acid. The solution, on being mixed with a stronger acid, gradually deposits the leucoturic acid, more quickly, however, if the sides of the vessel are rubbed with a glass rod. From the solution in *Potash*, the acid is separated in its original state by addition of a stronger acid.

The aqueous solution of the ammonia-salt forms, with nitrate of *silver*, a white precipitate, which gradually decomposes and turns brown, and when boiled with the watery liquid, deposits metallic silver without evolution of gas, but with formation of oxalic acid (Schlieper).

Lantanuric Acid. C^6NH^4,O^6?

SCHLIEPER (1848). *Ann. Pharm.* 67, 216.

Formation. By the oxidation of uric acid by a mixture of potash and ferricyanide of potassium.

Preparation. When pulverized ferricyanide of potassium is added by small portions to a solution of 10 pts. (1 At.) uric acid in 300 pts. of water containing potash at 20°, the ferricyanide quickly dissolves as ferrocyanide, and throws down acid urate of potash in thick white flakes. From this time forth, the liquid is mixed, alternately with potash till the flakes are dissolved, and with ferricyanide of potassium till they reappear, the alternations being made less frequently towards the end of the process, when the decomposition slackens, but continued till hydrochloric acid, added to a sample of the liquid, no longer throws down uric acid. — For this purpose, 41 pts. (2 At.) ferricyanide of potassium and 20·5 pts. (6 At.) hydrate of potash are used; therefore 2 At. O are transferred to 1 At. uric acid. — The liquid is then nearly neutralized with nitric acid (an excess would decompose the ferrocyanide of potassium), whereupon a very large quantity of carbonic acid is evolved, even if the potash was quite free from it, and the process was conducted out of contact of air; the liquid soon becomes reddish, and continues for several days, to deposit crystals of *allantoïn* and a small quantity of brick-red flakes, whereupon it recovers its yellow colour. (These brick-red flakes dissolve readily in ammonia or in potash; but the resulting reddish yellow solution yields but a small light yellow precipitate with acids. Their solution in potash assumes a pale yellow colour when boiled, and gives off ammonia, after which it no longer yields a precipitate with acids. They dissolve, with light yellow colour, very sparingly in cold, but abundantly in hot water, which then on cooling yields a sulphur-yellow deposit). — The yellow liquid separated from the red flakes and from the allantoïn, is supersaturated with nitric acid (to prevent the precipitation of an organic lead-salt); the ferrocyanide of potassium completely precipitated by nitrate of lead; the liquid freed from lead-oxide by sulphate of potash; the filtrate (which contains no oxalic acid) exactly neutralized with potash; the greater part of the nitre, together with a little remaining allantoin, removed by evaporation and crystallization; the mother-liquor considerably concentrated; and the rest of the nitre, together with the gummy neutral *lantanurate of potash*, precipitated from it by absolute alcohol. (The alcoholic solution still contains a small quantity of nitrate of urea). — 2. The process is commenced in the same manner; but the liquid, after the decomposition of the uric acid, instead of being treated with nitric acid, is nearly neutralized at a boiling heat with sulphuric acid; then evaporated, during which it constantly emits an ammoniacal odour; the greater part of the ferrocyanide of potassium crystallized out; the mother-liquor evaporated; the remainder of the ferrocyanide of potassium, together with the sulphate of potash, precipitated from it by alcohol; the precipitate boiled with alcohol; the whole of the alcoholic liquids evaporated, till the allantoïn crystallizes out; the mother-liquor evaporated to a viscid syrup; the syrup dissolved in water; and the lantanurate of potash, together with a very small quantity of oxalate,

precipitated in thick white flakes by absolute alcohol. — (If the liquid be neutralized with acetic acid, instead of nitric or sulphuric acid, the acetate of potash exerts during the evaporation (a large quantity of acetate of ammonia then volatilizing) a further decomposing action on the first formed decomposition-products, just as free potash would, and the final product is neither allantoïn, nor lantanuric acid, but oxalic acid).

The impure lantanurate of potash obtained by (1) or (2) is dissolved in water, mixed with acetate of lead, and filtered from the precipitate consisting chiefly of oxalate of lead; the lantanurate of lead precipitated from the filtrate by ammonia; washed, suspended in water, and decomposed by sulphuretted hydrogen; and the filtrate evaporated.

Properties. Gummy mass, easily soluble in water, insoluble in alcohol; its solution reddens litmus.

Lantanurate of Potash. — *a. Neutral.* — The potash-salt *b* dissolved in water and neutralized by potash, yields on evaporation a viscid syrup, which is precipitated by alcohol in thick white flakes, and is not reconverted into the crystalline salt *b* by stronger acids.

b. Hyperacid. — When the crystals obtained in the first method of preparing lantanuric acid are dissolved in cold potash to purify them from allantoïn, and the filtrate instantly supersaturated with acetic acid, the greater part of the allantoïn crystallizes out; and on separating the liquid from the crystals and evaporating to a syrup, the portion which remains in solution acts upon the acetate of potash in such a manner, as to form acetate of ammonia, which escapes, and lantanurate of potash. If, therefore, the syrup be dissolved in a small quantity of water, mixed with a quantity of alcohol just sufficient to produce turbidity, and this turbidity removed by the further addition of a small quantity of water, the mixture, when left for some time in a cool place, deposits crystalline crusts, which are increased by frequently adding small quantities of alcohol, till the liquid has lost its acid reaction. The crystals are purified by dissolving them several times in water, filtering from a yellow substance, and crystallizing. — Hard crystalline crusts, consisting of white strongly lustrous tables, which redden litmus strongly. — They give off 11·15 p.c. (4 At.) water at 100°. — They dissolve in 9 to 10 pts. of cold water, much more readily in hot water, from which they again separate slowly. The aqueous solution mixed with alcohol becomes milky, but afterwards clear, and forms small needles.

	Crystals.		Schlieper.	
			a.	*b.*
KO	47·2	15·42	14·22	14·22
12 C	72·0	23·51	22·65	22·65
4 N	56·0	18·29	19·63	17·47
11 H	11·0	3·59	4·09	4·09
15 O	120·0	39·19	39·41	41·57
	306·2	100·00	100·00	100·00

$C^6N^2H^3KO^6 + C^6N^2H^4O^6 + 4Aq$. (Gm.) — Schlieper, who gives the formula, $KO,C^6N^2H^4O^6 + HO,C^2N^2H^4O^6 + 4Aq$, had not correctly calculated the quantity of nitrogen found in analysis *b*, an error which the author has corrected in column *a* (Gm.). [In a subsequent communication (*Ann. Pharm.* 73, 225), Schlieper admits this error of calculation, but at the same time corrects another error, which compensates the former; he therefore adheres to his previous formula.]

Lantanurate of Lead. — Precipitated on adding ammonia to an aqueous mixture of neutral or acid lantanurate of potash, and neutral acetate of lead (*vid. sup.*). — White shining powder, insoluble in cold water and alcohol, sparingly soluble in hot water, easily in acetic acid and basic acetate of lead.

	Dried at 100°.		Schlieper.
2 PbO	224	69·57	67·27
6 C	36	11·18	10·28
2 N	28	8·69	7·83
2 H	2	0·62	1·17
4 O	32	9·94	13·45
$C^6N^2H^2Pb^2O^6$	322	100·00	100·00

[In assuming the formula $C^6N^2H^2Pb^2O^6$, it has been supposed that the salt analyzed by Schlieper was not dried at 100° for a sufficiently long time. If this supposition be correct — and without it, the analyses of the lead-salt and the acid potash-salt cannot be made to agree — lantanuric acid must be regarded as a bibasic acid = $C^6N^2H^4,O^6$, and its potash-salt as analogous to hyperacid oxalate of potash (p. 126) Gm.]

The aqueous mixture of the acid potash-salt with neutral acetate of lead, yields on addition of alcohol, white flakes probably consisting of an *acid lead-salt.*

The aqueous mixture of the acid potash-salt with nitrate of *silver* forms with ammonia a thick, white, flocculent precipitate, which is not altered by boiling with water, and, after drying at 100°, forms a white powder containing 52·93 p.c. silver (Schlieper).

Allanturic Acid. $C^6N^2H^4O^6 = C^6NAdH^2O^3,O^4$?

Pelouze. (1842). *N. Ann. Chim. Phys.* 6, 71; also *Ann. Pharm.* 44, 106; also *J. pr. Chem.* 28, 18.

Formation. By decomposing allantoïn with nitric acid or peroxide of lead; by boiling it with other strong acids or even with water; or by heating it *per se;* — also by decomposing uric acid with chlorine or nitric acid.

Preparation. Allantoïn is dissolved in nitric acid at 100°; the solution evaporated to dryness; the residue dissolved in a small quantity of water containing ammonia; the solution precipitated by alcohol; and the viscid precipitate redissolved in water and reprecipitated by alcohol, in order to extract all the urea and nitrate of ammonia. [Does not any ammonia remain with it?]

Properties. White, slightly acid.

According to Pelouze, the acid dried *per se* = $C^{16}N^4H^7O^9$; according to Gerhardt, = $C^6N^2H^4O^6$. No analysis is given.

The acid deliquesces in the air.

Its aqueous solution forms with acetate of lead and nitrate of silver, thick white precipitates, which dissolve in excess of the allanturic acid, and also of the metallic salts. The precipitate formed with nitrate of silver is greatly increased by addition of ammonia (Pelouze).

Diffluan

SCHLIEPER. (1845). *Ann. Pharm. 56, 5.*

Diffluan, from its tendency to deliquesce; therefore not *Difluan*. — Produced together with leucoturic acid, by continued boiling of an aqueous solution of alloxanic acid. The liquid finally evaporated to a syrup, after frequent renewal of the water, deposits the leucoturic acid on addition of cold water; and the filtrate mixed with a large excess of absolute alcohol, immediately deposits the diffluan in large white flakes, which must be quickly collected on a filter out of contact with the air, washed with absolute alcohol, then with ether, and dried in vacuo over oil of vitriol. The alcoholic filtrate, slowly evaporated to one-half, separated from a few crystalline crusts of another body formed over-night, and completely evaporated, yields, on addition of alcohol, a large additional quantity of diffluan.

Loose, white, somewhat aggregated powder, which melts at 100°, giving off alcohol and water with strong intumescence, and remains in the form of a transparent, brittle, vitreous gum, which admits of being rubbed to a white powder. Not crystallizable. Tastes sharp, bitter, and saline. Reddens litmus slightly.

			Schlieper at 100°.
6 C	36	33·33	32·69
2 N	28	25·93	25·70
4 H	4	3·70	3·89
5 O	40	37·04	37·72
	108	100·00	100·00

Diffluan, in all its relations, appears to be identical with allanturic acid. As it cannot be purified by crystallization, the substance analyzed by Schlieper may have contained a compound which diminished the amount of oxygen (Gerhardt, *N. J. Pharm.* 9, 233). — Diffluan probably contains 8 C instead of 6 C, inasmuch as alloxan, which contains 8 C, may be prepared from it (Gm.).]

Diffluan is decomposed with effervescence by hot nitric acid, forming alloxan, but neither alloxanic nor parabanic acid. It is gradually decomposed by cold potash-ley, yielding free ammonia and a large quantity of oxalic acid.

Diffluan deliquesces very rapidly in the air and forms a syrup. The aqueous solution may be boiled without decomposing. It is precipitated by alcohol in white flakes. If its acid reaction is neutralized by a drop of ammonia, the ammonia is given off completely again on evaporation.

Diffluan dissolved in water forms with neutral acetate of lead, a scanty precipitate soluble in excess of the lead-solution. The liquid separated from the precipitate, forms with ammonia a copious white precipitate which contains 71 p.c. oxide of lead; and after being washed with water, suspended in water, decomposed by sulphuretted hydrogen, filtered, and evaporated, yields a liquid from which alcohol precipitates unaltered diffluan, proving that this compound is not an ammoniacal salt.

With nitrate of silver, aqueous diffluan forms a precipitate, containing constantly 45·5 p.c. oxide of silver, a quantity which certainly does not agree with the above formula of diffluan, $C^6N^2H^4O^5$ (Schlieper).

γ. *Nitrogen-nucleus.* $C^6N^3H^3$.

Cyanuric Acid. $C^6N^3H^3,O^6$.

SCHEELE. *Opuscula*, 2, 177.
PEARSON. *Scher. J.* 1, 67.
WILLIAM HENRY. *Thomson Syst. de Chim. trad. p. Riffault*, 1818, 2, 198.
CHEVALLIER & LASSAIGNE. *Ann. Chim. Phys.* 13, 155; also *J. Pharm.* 6, 58; also *Schw.* 29, 357; also *N. Tr.* 5, 1, 174.
SERULLAS. *Ann. Chim. Phys.* 38, 379; also *N. Tr.* 18, 2, 146.
WÖHLER. *Pogg.* 15, 622.
LIEBIG & WÖHLER. *Pogg.* 20, 369; also *Mag. Pharm.* 33, 137.
LIEBIG. *Ann. Pharm.* 26, 121 and 145.
WÖHLER. *Ann. Pharm.* 62, 241.

Cyanursäure, Brenzharnsäure, Cyanurensäure, Acide pyro-urique, Acide cyanurique; for a time also, *Cyänsaure, Acide cyanique.*

Discovered by Scheele, who obtained it as a sublimate by the dry distillation of uric acid, and regarded it as similar to succinic acid. Pearson found it to resemble benzoic acid; Fourcroy regarded it as slightly altered uric acid; W. Henry, as a peculiar acid, a view which was confirmed by subsequent investigation. — By decomposing fixed chloride of cyanogen with water, Serullas, in 1828, obtained an acid which he regarded as C^2NHO^3, and named cyanic acid; and Wöhler, in 1829, showed that this acid was identical with pyro-uric acid, and was also obtained as a residue by heating urea. Subsequently, Liebig & Wöhler, in 1830, discovered the true composition of the acid and many of its chemical relations.

Formation. 1. By the dry distillation of uric acid (Scheele). — 2. By heating urea to a certain point (Wöhler, VII, 366). — In the decomposition of urea by hydrochloric acid (De Vry), or by chlorine (Wurtz). — 3. In the decomposition of fixed chloride of cyanogen, $C^6N^3Cl^3$, by water (Serullas):

$$C^6N^3Cl^3 + 6HO = C^6N^3H^3O^6 + 3HCl.$$

4. By boiling melamine with nitric acid, or cyanilic acid with oil of vitriol (Liebig, *Pogg.* 24, 583 and 603). — 5. By boiling 1 pt. of ammelide for six hours with 50 pts. of water and a quantity of phosphoric, sulphuric, or nitric acid, about sufficient to dissolve the ammelide, the ebullition being continued till the liquid is no longer precipitated by ammonia, after which it will yield by evaporation, beautiful crystals of cyanuric acid. Also by boiling 1 pt. of ammelide for an hour with 10 pts. of dilute potash (Knapp, *Ann. Pharm.* 21, 245). — 6. By the action of aqueous hypochlorous acid on hydrocyanic acid (Balard).

Preparation. When uric acid is subjected to dry distillation, cyanurate of ammonia partly sublimes, and partly passes over towards the end, together with the watery liquid. To free it from empyreumatic oil,

Scheele subjects it to a second distillation. — Pearson purifies it by sublimation, or by crystallization from the hot aqueous solution. — Chevallier & Lassaigne dissolve the sublimate in hot water; precipitate the solution by subacetate of lead; wash the precipitate with boiling water, decompose it, diffused in water, with sulphuretted hydrogen; and evaporate the filtrate to the crystallizing point. They likewise dissolve the liquid which has passed over and subsequently solidified, in hot water (whereupon small quantities of hydrocyanic acid and ammonia volatilize); filter from the tarry empyreumatic oil; evaporate to the crystallizing point; dissolve the resulting crystals in water; digest the solution with animal charcoal; and treat the still yellow crystals thus obtained, with basic acetate of lead and sulphuretted hydrogen, as above. — The whole of the crystals are freed from their yellow colour by digestion with animal charcoal.

2. Solid chloride of cyanogen is boiled with a large quantity of water in a flask provided with a long neck, the solid chloride of cyanogen which sublimes in the neck, being continually returned to the liquid by agitation, till the odour of chlorine of cyanogen is no longer perceptible; the liquid placed in a basin and evaporated nearly to dryness at a gentle heat, the greater part of the hydrochloric acid then escaping; the crystallized cyanuric acid washed on a filter with small quantities of cold water, till the water gives, with nitrate of silver, only a slight precipitate which dissolves in nitric acid, whereas a small quantity of ammonia increases the turbidity; the acid then dissolved in boiling water; and the filtrate evaporated to a certain point, and left to crystallize. — Cyanuric acid may also be obtained from cyanurate of baryta, by decomposing the aqueous solution of that salt with an exactly equivalent quantity of sulphuric acid. — Or, the wash-water of solid chloride of cyanogen (p. 464) which contains solid chloride of cyanogen, cyanuric acid, hydrochloric acid, and oil of chloride of cyanogen, may be evaporated to dryness, and the yellowish residue freed from the yellow colouring matter, either by extracting the latter with warm absolute alcohol, or decomposing it by boiling down three times with nitric acid, after which the residue is dissolved in hot water, filtered, and left to crystallize (Serullas). — 3. Urea is heated till it ceases to give off ammonia; the residue dissolved in boiling water, and the filtrate left to crystallize by cooling (Wöhler, VII, 366.) As the urea-residue may still contain ammonia and still exhibit colour, it must be dissolved in hot oil of vitriol; nitric acid dropped into the solution till all effervescence ceases and the solution is decolorized; and, after cooling, the cyanuric acid, precipitated from it by water; it is then obtained as a snow-white crystalline powder;—or it may be dissolved in boiling hydrochloric acid, which will deposit the cyanuric acid as it cools; — or the pulverized residue may be suspended in water, and chlorine passed through the liquid, whereupon the residue dissolves, forming solutions which deposit cyanuric acid in proportion as the chlorine escapes (Wöhler & Liebig). — 4. Pulverized urea is saturated with dry hydrochloric acid gas; the compound heated in the oil-bath, to 145°, at which temperature it begins to decompose; then taken out, whereupon violent decomposition takes place, and the temperature of the mass rises to 200°; and the residue dissolved in hot water, which on cooling, deposits white cyanuric acid, whilst sal-ammoniac remains in the solution. If the mass were left in the oil-bath, the compound $C^6N^4H^4O^4$ (VII, 369) would be obtained, instead of cyanuric acid.) (De Vry, *Ann. Pharm.* 61, 248. — 5. Dry

chlorine gas passed into melted urea produces strong intumescence and evolution of copious white fumes, the products of the action consisting of nitrogen, hydrochloric acid gas, sal-ammoniac, and cyanuric acid:

$$3C^2N^2H^4O^2 + 3Cl = N + HCl + 2NH^4Cl + C^6N^3H^3O^6.$$

If the greater part of the sal-ammoniac be dissolved out of the cooled residue by a small quantity of cold water, the cyanuric acid remains in the form of a white powder, which may be purified by solution in hot water and crystallization (Wurtz, *Compt. rend.* 24, 436).

The crystals of the acid obtained from the aqueous solution still require to be freed from their water of crystallization by gentle heating or by sublimation, or by solution in hot oil of vitriol or hydrochloric acid, and cooling.

Properties. White effloresced mass, or after sublimation, delicate needles (Chevallier & Lassaigne; Serullas); or, when crystallized from solution in oil of vitriol or hydrochloric acid, obtuse square-based octohedrons (Wöhler). Fuses when heated (Chev. & Lass.). Reddens litmus pretty strongly (Chev. & Lass.; Serullas). Inodorous, even in the state of vapour; has a somewhat acid taste (Scheele); sharp and bitter (Pearson); cooling and bitter (W. Henry). Given in a dose of two grains to a rabbit, it produces no particular effect (Serullas).

	Dried at 100°.			Liebig & Wöhler.	Chev. & Lass.
8 C	36	27·91	60·50		28·29
3 N	42	32·56			16·84
3 H	3	2·32	2·39		10·00
6 O	48	37·21	37·11		44·32
$C^6N^3H^3,O^6$	129	100·00	100·00		99·45

According to the radical-theory, the formula is $3HO,C^6N^3O^3$ (Liebig): $2HO, C^6N^3HO^4$ (Wöhler).

Decompositions. 1. The vapour of the acid passed through a red-hot tube, is resolved into charcoal, oil, carbonate of ammonia and carburetted hydrogen gas (Chev. & Lassaigne). — 2. When heated alone to the boiling point, it is converted, without leaving a carbonaceous residue, into vapour of cyanic acid, each 1 At. of cyanuric acid splitting up into 3 At. cyanic acid (Liebig & Wöhler):

$$C^6N^3H^3O^6 = 3 . C^2NHO^2.$$

The volatilization takes place somewhat above 360°, and the acid when gently heated, sublimes without decomposition in delicate needles, whereas if too much heat be applied, a residue of charcoal is left (Serullas). Chevallier & Lassaigne likewise obtained a sublimate consisting of delicate needles, and Wöhler obtained a white mealy powder, having partly a delicate crystalline texture, which dissolved very slowly in boiling water. All these sublimates doubtless consist of cyamelide, into which the volatilized cyanic acid has been converted (p. 462). — Cyanuric acid mixed with nitrate of ammonia decomposes at a much lower temperature than when heated alone (Pelouze, *N. Ann. Chim. Phys.* 6, 69). — 3. When heated in the moist state, it forms carbonic acid and ammonia, in quantity proportionate to the water which is present (Serullas):

$$C^6N^3H^3O^6 + 6HO = 6CO^2 + 3NH^3.$$

4. It is not decomposed by boiling [for a short time] with nitric acid (Pearson, Chev. & Lassaigne, Serullas), or with oil of vitriol (Serullas); but when heated for a longer time with these acids, it is resolved into carbonic acid and ammonia (Liebig, *Chim. org.*). — 5. When fused with potassium, it forms cyanide of potassium and potash (Serullas). Perhaps in this manner:

$$C^6N^3H^3O^6 + 6K = 3C^2NK + 3(KO,HO).$$

Combinations. A. With *Water.* — *a. Hydrated Crystals.* — The acid crystallizes from its aqueous solution in prisms belonging to the right prismatic system (Wöhler); in transparent, colourless, shining rhombs (Serullas). The finest crystals are obtained by evaporating the boiling, saturated aqueous solution to one-half at a temperature between 60° and 80°, and leaving the liquid to cool slowly (Liebig & Wöhler). The crystals effloresce in the air, and give off all their water of crystallization when heated (Wöhler).

			Liebig & Wöhler.
$C^6N^3H^3O^6$	129	78·18	78·44
4 Aq	36	21·82	21·56
$C^6N^3H^3O^6$	165	100·00	100·00

b. The acid dissolves in 40 pts. of cold water (Chev. & Lass.) more copiously in hot water (Scheele, Serullas.)

B. *With Mineral Acids.* — The acid dissolves in boiling oil of vitriol, forming a colourless liquid, from which it is precipitated by water (Serullas). — It also dissolves in hot nitric acid (Chev. & Lassaigne; Serullas).

C. *With Salifiable Bases,* forming the *Cyanurates.* Cyanuric acid is tribasic, according to Liebig; bibasic according to Wöhler. The cyanurates do not detonate when heated. Cyanurate of potash (*q. v.*) is converted by heat into cyanate (Liebig & Wöhler). — Cyanurate of potash ignited with potassium is converted into cyanide of potassium (Serullas). [Perhaps with evolution of hydrogen and formation of potash]. Cyanurates which are soluble in water, are not decomposed by boiling the solution. The solution forms with silver-salts, a white precipitate soluble in nitric acid (Serullas).

Cyanurate of Ammonia. — Sublimes in an impure state, in the dry distillation of uric acid, forming tufts of needles which redden litmus and have a slightly bitter taste (Chev. & Lassaigne). This sublimate is regarded by Kodweiss (*Pogg.* 19, 11) as cyanurate of urea. — The aqueous solution neutralized with ammonia while warm, yields on cooling white, shining prisms, which effloresce in the air, with loss of ammonia, and likewise give up ammonia to cold water (Berzelius, *Lehrb.*).

Cyanurate of Potash. a. Bipotassic. — $C^6N^3HK^2O^6$. — Precipitated in white four-sided tables and needles, on mixing aqueous cyanuric acid with excess of alcoholic potash (Liebig & Wöhler, *Pogg.* 20, 377).—A solution of 1 pt. ammelide in 10 pts. dilute potash boiled for an hour and cooled, yields the salt in delicate silky needles, which thicken the liquid napp, *Ann. Pharm.* 21, 245). The salt heated alone is resolved, with ng ebullition, into cyanic acid which volatilizes, and is afterwards con-

verted into cyamelide and 77·85 p.c. cyanate of potash (Liebig, *Ann. Pharm.* 26, 121). Calculation gives 79·06 per cent:

$$C^6N^3HK^2O^6 = 2C^2NKO^2 + C^2NHO^2.$$

The aqueous solution deposits by evaporation the following salt *b*, while free potash remains in the mother-liquor (Liebig & Wöhler):

$$C^6N^3HK^2O^6 + HO = C^6N^3H^2KO^6 + KO.$$

Acetic acid added to the aqueous solution throws down the crystalline salt *b* (Liebig): so likewise does a small quantity of nitric acid; but a larger quantity throws down pure cyanuric acid (Knapp).

Crystallized,			Or:			Liebig.
6 C	36·0	17·52	$C^6N^3O^3$	102·0	49·66	
3 N	42·0	20·45	HO	9·0	4·38	5·02
H	1·0	0·49	2 KO	94·0	45·96	45·65
2 K	78·4	38·17				
6 O	48·0	23·37				
$C^6N^3HK^2O^6$	205·4	100·00	$2KO,HO,C^6N^3O^3$	205·4	100·00	

b. Monopotassic. $C^6N^3H^2K,O^6$. — 1. Obtained in shining white cubes by dissolving cyanuric acid in aqueous potash and evaporating, even if the solution contains excess of potash (Liebig & Wöhler). — 2. Campbell (*Ann. Pharm.* 28, 57) treats ferrocyanide of potassium, roasted in the manner which he recommends for the preparation of cyanate of potash (VIII, 66), with a small quantity of water, mixes the cold filtrate containing cyanate of potash with hydrochloric acid, and purifies the cyanurate of potash thereby precipitated by recrystallization from hot water. — The crystals when fused, are resolved, without blackening, into cyanic acid vapour which condenses as cyamelide, and cyanate of potash (Liebig & Wöhler):

$$C^6N^3H^2KO^6 = C^2NKO^2 + 2C^2NHO^2.$$

Liebig obtained by this decomposition 48 p. c. cyanate of potash; calculation requires 48·56 per cent. — The salt when ignited with hydrate of potash is converted into 3 At. cyanate of potash (Liebig):

$$C^6N^3H^2O^6 + 2(KO,HO) = 3C^2NKO^2 + 4HO.$$

It dissolves in water less easily than *a*:

			Or:			Liebig.
6 C	36·0	21·53	$C^6N^3O^3$	102·0	61·01	
3 N	42·0	25·12	2 HO	18·0	10·76	
2 H	2·0	1·20	KO	47·2	28·23	27·72
K	39·2	23·44				
6 O	48·0	28·71				
$C^6N^3H^2KO^6$	167·2	100·00	$KO,2HO,C^6N^3O^3$	167·2	100·00	

Cyanurate of Soda. — Uncrystallizable, readily soluble in water (Chev. & Lassaigne).

Cyanurate of Baryta. — *a. Bibarytic.* $C^6N^3HBa^2,O^6$. — Precipitated in the crystalline form from a boiling aqueous mixture of cyanuric acid and chloride of barium, on addition of ammonia, or from a mixture of aqueous cyanuric acid and excess of baryta-water; there is however considerable difficulty in separating it from the monobarytic salt *b*, and from

carbonate of baryta The crystalline powder begins to give off water at 200°, and at 250°, the loss amounts to 6·45 per cent; at a higher temperature it gives off ammonia, then cyanic acid, and ultimately fuses, and is converted into the salt *b*. The baryta in the crystals amounts to 53·19 per cent (Wöhler). — Chevallier & Lassaigne obtained the salt in the form of a powder sparingly soluble in water.

b. Monobarytic. $C^6N^3H^2Ba,O^6$. — Cyanurate of ammonia does not precipitate baryta-water (Chev. & Lassaigne); cyanuric acid forms no precipitate with hydrochlorate or acetate of baryta (Wöhler). — Baryta-water is dropt into a boiling solution of cyanuric acid, as long as the resulting precipitate redissolves and the still acid liquid exhibits turbidity from separation of a powder; the liquid then kept for an hour at 60°, so that no free cyanuric acid may be deposited; then thrown while still hot upon a filter, and thoroughly washed. Short transparent needles, containing 35·44 p.c. baryta. Their water begins to escape at 200°, and is entirely given off at 280°, amounting to 8.45 per cent. At a higher temperature, the crystals, which have become milky, are decomposed (Wöhler).

a. Bibarytic.	*Crystals at* 100°.		Wöhler.
6 C	36·0	12·36	
3 N	42·0	14·42	
4 H	4·0	1·37	1·52
2 Ba	137·2	47·12	47·63
9 O	72·0	24·73	
$C^6N^3HBa^2O^6 + 3Aq$	291·2	100·00	

b. Monobarytic.	*Crystals at* 100°.		Wöhler.
6 C	36·0	16·78	
3 N	42·0	19·57	
4 H	4·0	1·86	
Ba	68·6	31·97	31·75
8 O	64·0	29·82	
$C^6N^3H^2BaO^6 + 2Aq$	214·6	100·00	

The salt *a* burnt with oxide of copper yields 13·71 p. c. (4 At.) water; when heated alone to 250°, it gives off only 6·45 (2 At.); hence one atom of the water of crystallization cannot be driven off by heat (Wöhler).

Cyanurate of Lime. — Crystallizes in nodules; has a sharp and bitter taste; fuses at a gentle heat; and solidifies on cooling, in a mass resembling yellow wax in consistence and colour. Contains 8·6 per cent of lime. Dissolves readily in water (Chevallier & Lassaigne).

Cyanurate of Lead. — $C^6N^3HPb^2O^6 + PbO + 2$ Aq. The potash-salt precipitates basic but not neutral acetate of lead. The precipitate contains 71·5 p.c. oxide of lead (Chev. & Lassaigne). Cyanuric acid does not precipitate sugar of lead mixed with acetic acid (Wöhler). 1. Basic acetate of lead is dropped into a solution of cyanuric acid saturated at a boiling heat, the acid being in excess. — 2. A boiling aqueous solution of cyanuric acid is added in excess to an aqueous solution of neutral acetate of lead. — 3. Neutral acetate of lead is precipitated by cyanurate of ammonia. — 4. Recently precipitated carbonate of lead is added to boiling aqueous cyanuric acid, which must be in excess. — Heavy crystalline precipitate, which, when examined by the microscope, is found to consist of transparent prisms with oblique terminal faces, and often united in hemitropic or fern-like groups. In the mass it has a yellowish colour. — At 100°, it begins to

give off water, and at 250°, the loss amounts to 1·94 p.c. (1 At.). The second atom of water does not go off till the salt is heated to a temperature at which it is decomposed, with evolution of a large quantity of ammonia. When burnt with oxide of copper, it yields 5·63 p.c. (3 At.) water. Heated to redness in a current of hydrogen, it gives off a large quantity of hydrocyanate of ammonia and urea, and leaves pure melted lead (Wöhler). It does not appear possible to form a cyanurate of lead with less than 3 At. lead.

	Crystals dried at 100°.			Wöhler.
3 PbO	336	72·26		72·47
6 C	36	7·74		7·99
3 N	42	9·03		
3 H	3	0·64		0·62
6 O	48	10·33		
$PbO,C^6N^3HPb^2O^6+2Aq$	465	100·00		

Bipotassic cyanurate forms a brownish yellow precipitate with ferric salts, — bluish white with cupric salts; — from mercurous or mercuric nitrate, it throws down white flakes soluble in nitric acid (Chev. & Lassaigne).

Cupric Cyanurate. — A definite salt appears difficult to obtain.

a. Recently precipitated cupric hydrate added by small portions to hot aqueous cyanuric acid till the liquid is saturated, forms a clear solution, and, on cooling, soon yields a bluish green crystalline precipitate, which assumes a fine blue colour at 100°, and at 250° gives off 9 p.c. water, and changes to pure green just like chromic oxide; from the results of analysis, it appears to be a mixed basic salt with more than 3 At. cupric oxide. — *b.* Crystallized cyanurate of ammonia dissolved in water forms with cupric sulphate a greenish blue amorphous precipitate, which, when heated, becomes crystalline, and assumes, first, a blue, then a green colour; it is free from ammonia, but contains sulphuric acid as an essential constituent. The liquid filtered from this precipitate, deposits crystallized cyanuric acid. — *c.* When aqueous solutions of cyanuric acid and cupric acetate saturated while hot, are boiled together for some time, a green precipitate is formed containing acetic acid in combination (Wöhler).

Bicupric Cyanurate with Ammonia. — A solution of cyanuric acid in very dilute ammonia, mixed while hot with a solution of cupric sulphate in very dilute ammonia, deposits on cooling, crystals which may be washed with water, inasmuch as they dissolve in it but sparingly. Small amethyst-coloured crystals, which, when examined by the microscope appear to be four-sided prisms, with two broader lateral faces, and bevelled with two faces. — The salt is permanent in the air, begins to give off ammonia at 100°, and at 230° assumes a dark olive-green colour, with loss of 14·85 per cent. At a still higher temperature, it suddenly becomes yellow, then takes fire, and glimmers away till it is converted into cupric oxide. It is free from sulphuric acid. Nearly insoluble in ammonia (Wöhler).

Dried at 100°.			Wöhler.	*Heated to* 230°.			Wöhler.
6 C	36	14·81	14·80	6 C	36	17·31	
5 N	70	28·81	26·85	4 N	56	26·92	
9 H	9	3·70	3·94	4 H	4	1·93	
2 Cu	64	26·34		2 Cu	64	30·77	30·87
8 O	64	26·34		6 O	48	23·07	
	243	100·00			208	100·00	

[The salt at 30° is probably = $2NH^3,C^6N^3HCu^2O^6 + 2Aq$. Wöhler supposes it to contain 1 At. water more (which however does not agree so well with his analysis), and writes: $2NH^3 + 2CuO,C^6N^3HO^4 + 3Aq$. He found in it 32·85 p.c. cupric oxide and 13·28 ammonia; calculation (243 : 34) gives for the latter 13·99 per cent.

The salt heated to 230° is probably = $NH^3,C^6N^3HCu^2O^6$. Wöhler supposes it to contain another atom of water (which however is less accordant with the analysis), and writes: $2CuO,NH^4O,C^6N^3HO^4$. He found it to contain 38·59 p.c. cupric oxide.]

If, in the preparation of the salt just described, a large excess of ammonia be avoided, and the two liquids be mixed boiling hot, a peach-blossom-coloured powder is precipitated, containing cupric but not cuprous oxide. Its azure-blue solution in concentrated ammonia immediately deposits crystals of a deep smalt-blue colour, which, when exposed to the air, give off ammonia, and soon recover their peach-blossom colour.

Cyanurate of Silver. — *a. With 3 At. Silver.* — When nitrate of silver is precipitated by cyanuric acid which is supersaturated with ammonia, and the copious pulverulent precipitate boiled for a quarter of an hour with the supernatant liquid, a precipitate of constant composition is obtained. This precipitate, after being washed with boiling water and dried, is snow-white; does not blacken by exposure to light; and may be heated to 300° without decomposition, merely giving off a small quantity of ammonia, in case it has not been washed with boiling water. After drying, it rapidly absorbs moisture from the air (Liebig, *Ann. Pharm.* 26, 123). The precipitate, when examined by the microscope, appears uniform and composed of very small prisms; even after washing with boiling water, it gives off ammonia, not only when acted upon by potash, but likewise when heated alone; from 100° to 300°, the loss of ammonia amounts to 2·9 per cent; the pale violet residue, when more strongly heated, decomposes with a hissing noise, leaving a residue of silver. The precipitate, before being heated, is perhaps a compound of the terargentic silver-salt with ammonia, part of which is given off below 100°, and the greater portion 2·9 (p.c.) between 100° and 300° (Wöhler).

	At 300°.			Liebig.	Wöhler.
6 C	36	....	7·84	8·08	8·40
3 N	42	....	9·15		
H	1	....	0·22	0·10	0·13
3 Ag	324	....	70·59	71·09	70·38
7 O	56	....	12·20		
$AgO,C^6N^3HAg^2O^6$	459	....	100·00		

Wöhler, and more especially Liebig, obtained less H than the formula requires; but Wöhler suggests, that at 300°, the acid of the salt undergoes a partial decomposition, which is indeed indicated by the violet colouring produced at that temperature. [It would be desirable on this account to ascertain whether, from the salt dried at 300°, the whole of the acid can be recovered in its unaltered state. If this were the case, we should have further to assume, that at a sufficiently high temperature, all the hydrogen in the salt is replaced, with formation of water, by the third atom of silver, and that $C^6N^3Ag^3O^6$ is produced, containing, according to calculation, 8·00 p.c. C, 9·33 N, 72·00 Ag, and 10·67 O. There are other cases in which it is necessary to suppose, that in an acid, such atoms of hydrogen as are not generally replaceable by metals, nevertheless do give place to a metal when the acid is acted upon at high temperatures by an excess of a metallic oxide the oxygen of which is loosely combined.

b. With 2 At. Silver. $C^6N^3HAg^2O^6$. — Free cyanuric acid does not precipitate nitrate of silver. — 1. Recently precipitated carbonate of silver is added to the boiling aqueous acid, in such proportion, that part of the

acid remains in the water in the free state above the salt which has been formed (Wöhler). — 2. Nitrate of silver is precipitated by cyanuric acid exactly saturated with ammonia. The liquid above the thick white curdy precipitate reddens litmus (Liebig & Wöhler). The solution of cyanurate of ammonia must be added by drops to that of the nitrate of silver, which must remain in excess. — 3. A boiling aqueous mixture of cyanuric acid and acetate of soda is dropped into a boiling dilute solution of nitrate of silver, which must remain in excess, to prevent admixture of the insoluble cyanurate of silver and sodium (Wöhler). — 4. A solution of cyanuric acid is mixed hot with a solution of acetate of silver, which should contain excess of acetic acid. This is the surest method of obtaining a pure salt (Wöhler). — Colourless crystalline powder which, under the microscope, appears to consist of transparent rhombohedrons. It is not blackened by light. Does not lose weight at 200°; above 200°, it assumes a light cinnamon colour, but loses not more than a few thousandths of its weight. At a higher temperature, it emits a strong odour of cyanic acid, assumes a dark violet colour, and is finally decomposed with a glimmering light, leaving metallic silver. Dissolves in nitric acid, with liberation of cyanuric acid. Insoluble in water and in acetic acid.

Dried between 100° *and* 200°.				Wöhler.
6 C	36	10·50		10·62
3 N	42	12·24		
H	1	0·29		0·34
2 Ag	216	62·97		62·58
6 O	48	14·00		
$C^6N^3HAg^2O^6$	343	100·00		

The salt prepared by (1), perhaps not so thoroughly dried, was formerly found by Liebig & Wöhler to contain 60 per cent. of silver. — The salt dried at 290° contains 63·54 p.c. silver (Wöhler).

Cyanurate of Silver with Ammonia. — The last-described salt digested with strong ammonia, takes up ammonia, whereby it is altered in appearance, but does not dissolve. The compound begins at 60° to give off its ammonia, which escapes completely between 200° and 300° (Wöhler).

Dried at 20°.			Wöhler.
6 C	36	9·55	
5 N	70	18·57	
7 H	7	1·86	
2 Ag	216	57·29	57·05
6 O	48	12·73	
$2NH^3,C^6N^3HAg^2O^6$	377	100·00	

Cyanurate of Silver and Ammonium. — The liquid filtered at a boiling heat from the precipitate of terargentic cyanurate (p. 456), deposits on cooling a powder which after washing must be dried without heat. The same salt is obtained on mixing the hot solutions of cyanurate of ammonia and nitrate of silver, and boiling the precipitate with the liquid. The white powder, when examined by the microscope, appears to consist of long delicate needles. It gives off ammonia when treated with potash; also when merely heated, at a temperature below 100°. After being heated for two hours to 259°, it loses 7 per cent, but nevertheless remains white. At a higher temperature, it fumes strongly, assumes a violet colour, and finally leaves metallic silver amounting to

53·33 per cent of the salt previously heated to 250°, and therefore 49·40 per cent of the cold-dried salt (Wöhler). According to Wöhler's supposition, the cold-dried salt = $3NH^4O,C^6N^3HO^4 + 3AgO,C^6N^3HO^4$; the salt by being heated to 250°, loses therefore $2NH^3 + HO$, and is then = $NH^4O,HO,C^6N^3HO^4 + 3AgO,C^6N^3HO^4$. — Laurent (*N. Ann. Chim. Phys.* 23, 114), gives different formulæ for these compounds of ammonia, silver-oxide and cyanuric acid.

Cyanurate of Silver and Potassium. — Biargentic cyanurate is not decomposed by boiling with potash, but takes up a portion of the potash. The compound fuses, with decomposition and ebullition, and leaves a mixture of carbonate and cyanate of potash, together with nearly 60 p.c. silver (Wöhler). If this compound consisted of 1 At, biargentic cyanurate with 1 At. potash, it should have yielded 55 p.c. silver; it probably contained a portion of undecomposed biargentic cyanurate (Wöhler).

Cyanurate of Silver and Lead. — When terplumbic cyanurate is boiled with a large excess of nitrate of silver, till its appearance is quite changed, a filtrate is obtained containing a large proportion of lead; and on the filter there remains a salt in which 2 At. lead are replaced by 2 At. silver = $PbO,C^6N^3HAg^2O^6 + Aq$. After drying at 100°, it yields, when reduced by hydrogen, 69·64 p.c. of an alloy consisting of 45·94 silver and 23·70 lead (Wöhler).

Cyanurate of Urea? — By dissolving cyanuric acid in a boiling saturated solution of urea, and cooling the liquid, delicate needles are obtained (Kodweiss, *Pogg.* 19, 11).

Cyanuric acid is insoluble in alcohol (Serullas). It dissolves in boiling alcohol of 36° Bm. and is deposited in small granules as the liquid cools (Chevallier & Lassaigne).

Conjugated Compounds of Cyanuric Acid?

Cyanurate of Methyl. $C^{12}N^3H^9O^6 = 3C^2H^3O,C^6N^3O^3$?

WURTZ (1848). *Compt. rend.* 26, 369; also *J. pr. Chem.* 45, 316:— More fully, *N. Ann. Chim. Phys.* 42, 62.

Sublimes when sulphomethylate of potash is distilled in the oil-bath with bipotassic cyanurate of potash or with cyanate of potash, and is purified by crystallization from alcohol.

Small colourless prisms, which melt at 175° to 178° and boil at 274°. Vapour-density = 5·98 (Wurtz). — The boiling-point of this compound appears therefore to be higher than that of cyanurate of ethyl (Gerhardt, *N. J. Pharm.* 13, 456).

	¶ *Calculation.*		Wurtz (*mean*).			Vol.	Density.
12 C	72	42·10	42·12	C-vapour	12		4·9920
9 H	9	5·26	5·52	H-gas	9		0·6237
3 N	42	24·56	24·74	N-gas	3		2·9116
6 O	48	28·08	27·62	O-gas	3		3·3279
$3C^2H^3O,C^6N^3O^3$	171	100·00	100·00		2		11·8552
					1		5·9276

Cyanurate of methyl distilled with aqueous potash yields methylamine and carbonate of potash (Wurtz, *Ann. Pharm.* 71, 332; *Chem. Soc. Qu. J.* 3, 92):

$$3C^2H^3O,C^6N^3O^3 + 6(KO,HO) = 6(KO,CO^2) + 3C^2H^5N \text{ ¶}$$

Cyanurate of Ethyl. $C^{15}N^3H^{15}O^6 = 3C^4H^5O,C^6N^3O^3$?

WURTZ (1848). *Compt. rend.* 26, 368; also *J. pr. Chem.* 45, 316; *Ann. Pharm.* 71, 326; *Chem. Soc. Qu. J.* 3, 90. More fully: *N. Ann. Chim. Phys.* 42, 57.

Vinic or *Ethylic Cyanurate, Cyanuric Ether.*

A mixture of sulphovinate and bipotassic cyanurate of potash is distilled in the oil-bath, and the sublimate which collects in the neck of the retort and in the receiver, purified by crystallization from hot alcohol. — If cyanate of potash be used instead of cyanurate, a very irritating fluid mixture of cyanuric and cyanic ether distils over; and on distilling this mixture at a gentle heat, the cyanic ether, which boils at 60°, passes over, while the cyanuric ether remains and may be purified by crystallization from alcohol.

Shining prisms, which melt at 95°, to a colourless liquid heavier than water, and boiling at 253°, without a trace of decomposition. Vapour-density = 7·4.

	¶ *Calculation.*		Wurtz (*mean*).			Vol.	Density.
18 C	108	50·70	50·54	C-vapour	18		7·4480
15 H	15	7·04	7·04	H-gas	15		1·0395
3 N	42	19·72	20·02	N-gas	3		2·9116
6 O	48	22·54	22·40	O-gas	3		3·3279
$3C^4H^5O,C^6N^3O^3$	213	100·00	100·00		2		14·7670
					1		7·3835

Cyanuric ether continuously boiled with aqueous potash gives off ethylamine and leaves carbonate of potash (Wurtz, *Ann. Pharm.* 71. 328):

$$3C^4H^5O,C^6N^3O^3 + 6(KO,HO) = 6(KO,CO^2) + 3C^4H^7N. \P$$

From the analyses of these two cyanuric ethers, Wurtz regards it as proved that cyanuric acid is not bibasic but tribasic. It still, however, remains to be ascertained by the study of various reactions, whether, in the formation of these two compounds, changes do not take place, similar to those which occur in the formation of allophanic ether from alcohol and cyanic acid, and whether cyanuric acid and wood-spirit or alcohol can be recovered from them.

¶ This question has been taken up by Limpricht (*Ann. Pharm.* 74, 208), who maintains that Wurtz's cyanuric ether cannot contain either cyanuric acid or oxide of ethyl, inasmuch as it is resolved by potash, not into cyanuric acid and alcohol, in the manner of other compound ethers, but into carbonic acid and ethylamine. He finds that this decomposition is preceded by the formation of another body containing $C^{15}N^3H^{15}O^3$. The reaction is best observed by using baryta instead of potash. When cyanuric ether is boiled with baryta-water, it takes up 4 At. water, and gives up 3 At. carbonic acid to the baryta; and on removing the baryta and evaporating, there remains a turpentine-like body having the composition just mentioned. This liquid heated to 170°, partly distils without alteration, and is partly resolved (more quickly at 200°) into ethylamine and another less volatile compound, $C^{11}N^3H^{11}O^3$:

$$C^{15}N^3H^{15}O^3 = C^4H^7N + C^{11}N^3H^{11}O^3.$$

The last-mentioned compound is solid at ordinary temperatures; exhibits

neither acid nor alkaline reaction; melts at 106°; sublimes at about 250°; and when boiled with potash, is resolved into carbonic acid and ethylamine:

$$C^{11}N^2H^{11}O^3 + 3HO = 3CO^2 + 2C^4H^7N.$$

Limpricht has also obtained another compound, $C^{14}N^3H^{11}O^6 = 2C^4H^5O,HO,C^6N^3O^3$?, differing from Wurtz's cyanuric ether by C^4H^4, or by containing 1 At. H in place of 1 At. C^4H^3. This compound is obtained in the preparation of Wurtz's ether, passing over in fact, apparently in combination with methylamine, towards the end of the operation, when the heat becomes strong; in this state of combination, it is not crystallizable, and therefore remains in the mother-liquor of Wurtz's ether. It is decomposed by boiling with baryta-water, with evolution of methylamine; and on removing the baryta by means of sulphuric acid, the compound $C^{14}N^3H^{11}O^6$ crystallizes out in beautiful six-sided prisms with tetrahedral summits. This compound melts at 173°, and at a higher temperature sublimes without decomposition. It dissolves with tolerable facility in hot water, alcohol, and ether, and crystallizes from the ethereal solution in obtuse rhombohedrons. The aqueous solution has an acid reaction. The compound does not increase in weight by immersion, either in dry ammoniacal gas or in hydrochloric acid. It dissolves readily in ammonia, potash and baryta-water, crystallizing out again unaltered. The hot ammoniacal solution mixed with nitrate of silver deposits needle-shaped crystals of the compound $AgO,C^{14}N^3H^{10}O^5$; it is also precipitated by lead, copper and mercurous salts. The lead-compound heated with sulphovinate of potash yields Wurtz's cyanuric ether. The compound $C^{14}N^3H^{11}O^6$ fused with hydrate of potash gives off ethylamine. Like Wurtz's ether it cannot be decomposed into cyanuric acid and alcohol (Limpricht).

Gerhardt (*Compt. mensuels*, 1850, 309) remarks that Limpricht's first compound $C^{15}N^3H^{15}O^3$, may be neutral carbonate of ethylamine *minus* water, that is to say, *ethylamine-urea* $= C^{10}N^2H^{12}O^2$. For the second of the above compounds, $C^{11}N^2H^{11}O^3$, Gerhardt suggests as more probable the formula $C^6NH^5O^2$ [which would make it isomeric with cyanic ether]; it would then be produced from the former simply by abstraction of ethylamine; $C^{10}N^2H^{12}O^2 = C^4H^7N + C^6NH^5O^2$. The third compound, $C^{14}N^3H^{11}O^6$, Gerhardt regards as an *ethylocyanuric acid*, intermediate between Wurtz's cyanuric ether and the true but not yet discovered ethylocyanuric or cyanurovinic acid: thus:

$$C^6N^3H^3O^6 + C^4H^6O^2 - 2HO = C^{10}N^3H^7O^6 \text{ (Unknown)}.$$
$$C^6N^3H^3O^6 + 2C^4H^6O^2 - 4HO = C^{14}N^3H^{11}O^6 \text{ (Limpricht)}.$$
$$C^6N^3H^3O^6 + 3C^4H^6O^2 - 6HO = C^{18}N^3H^{15}O^6 \text{ (Wurtz)}.$$

The non-reproduction of cyanuric acid or alcohol from cyanuric ether by the action of alkalis is regarded by Gerhardt as affording no argument against the terbasic character of cyanuric acid; since, on similar grounds, we might refuse to consider hydrocyanic ether as an ethyl-compound, seeing that it is resolved by alkalis into ammonia and propionic acid.

Wurtz likewise observes that tribasic cyanuric ether is not the only solid product obtained by the action of cyanate of potash on the sulphovinate, compounds being sometimes formed differing therefrom in properties and composition. He did not however obtain these products in sufficient quantity to enable him to decide on their composition, or to study the conditions of their formation.

Tribasic cyanuric ether dissolves readily in alcohol, especially in strong alcohol. Water added to the alcoholic solution throws down cyanuric ether in the crystalline form; nevertheless it is soluble in water to a certain extent, especially when boiled therewith (Wurtz) ¶.

Compounds metameric with Cyanuric acid.

1. Cyanylic Acid. $C^6N^3H^3O^6 = C^6N^3H^3O^2,O^4$?

Liebig (1834). *Pogg.* 34, 599; also *Ann. Pharm.* 10, 32.

Mellone is dissolved in boiling nitric acid, either dilute or concentrated; the solution left to cool till it crystallizes; the crystals freed from nitric acid by cold water; and then recrystallized from hot water. Cyanuric acid is often mixed with the product, but always crystallizes out first.

The acid crystallizes in combination with water, in long, transparent, colourless, rhombic prisms, or in broad laminæ having a pearly lustre. *Fig.* 54. $u : u = 95° 36'$ and $84° 24'$; $i : i$ backwards $= 83° 24'$.

The crystals effloresce when exposed to the air.

The acid, like cyanuric acid, volatilizes in the form of cyanic acid, when heated. — By solution in oil of vitriol, and precipitation therefrom by water, it is converted into cyanuric acid, and no longer exhibits the pearly lustre above mentioned, after crystallization from water.

It dissolves in *Water* somewhat more readily then cyanuric acid; and the hot-saturated aqueous solution solidifies almost wholly in a laminated mass on cooling.

All the *Cyanylates, e. g.*, those of the six fixed alkalis, are completely decomposed by the stronger acids, so that as the liquid cools, the cyanylic acid crystallizes out in the free state.

Cyanylic acid neutralized witth ammonia, forms with nitrate of silver a white, tumefied precipitate, which, after drying, is pulverulent, amorphous, and contains 45·36 per cent. of silver; but the precipitate obtained with cyanylate of potash has the composition of cyanurate of silver, probably because the potash converts the cyanylic acid into cyanuric (Liebig).

Dried acid.				Liebig.
6 C	36	27·91		28·75
3 N	42	32·56		32·80
3 H	3	2·32		2·49
6 O	48	37·21		35·96
$C^6N^3H^3O^6$	129	100·00		100·00

Crystallized acid.			Liebig.
$C^6N^3H^3O^6$	129	78·18	79
4 Aq	36	21·82	21
$C^6N^3H^3O^6 + 4Aq$	165	100·00	100

Silver-salt prepared with Cyanylate of Ammonia.			Liebig.
C^6N^3	78	33·05	
2 H	2	0·85	
Ag	108	45·76	45·36
6 O	48	20·34	
$C^6N^3H^2AgO^6$	236	100·00	

2. Cyamelide. $C^3N^3H^3O^3 = C^3N^3H^3O^1,O^2$?

LIEBIG. *Mag. Pharm.* 29, 228. — *Pogg.* 15, 561.
LIEBIG & WÖHLER. *Pogg.* 20, 384.

Insoluble Cyanuric acid, Hypocyanic acid. — Discovered by Liebig in 1830.

Formed spontaneously from cyanic acid (p. 63). — Cyamelide is produced, not only when pure anhydrous or concentrated cyanic acid is left to itself, but likewise in a mixture of cyanates with concentrated acids, *e. g.* when cyanate of potash is triturated with fuming nitric or sulphuric acid, with crystallized oxalic or tartaric acid, or with concentrated acetic or hydrochloric acid. Thus, equal parts of cyanate of potash and crystallized oxalic acid triturated together, form a mixture which, when gently heated, gives off the odour of cyanic acid, becomes pasty, and then immediately solidifies to a mixture of cyamelide and oxalate of potash, which latter may be dissolved out from the cyamelide by boiling water.

White, solid, amorphous, inodorous.

Cyamelide, when somewhat strongly heated, is reconverted into cyanic acid and volatilizes. — Heated with oil of vitriol, it effervesces and is completely decomposed into carbonic acid and sulphate of ammonia:

$$C^3N^3H^3O^3 + 6HO = 6CO^2 + 3NH^3.$$

It is not decomposed by boiling with hydrochloric, nitric, or nitro-hydrochloric acid. — It dissolves in potash with tolerable facility, and without evolution of ammonia; and the solution when evaporated (whereupon carbonate of ammonia is evolved, a proof that cyanate of potash has likewise been formed) yields cyanurate of potash. Cyanuric acid may therefore be converted by heat into cyanic acid; and this acid changes spontaneously into cyamelide, which with potash reproduces cyanuric acid.

Cyamelide dissolves in *Ammonia*. — It does not dissolve in *Water* either cold or hot; but when boiled with water for some time, it is converted into a hydrate, which dissolves in small quantity, and separates again in white flakes on cooling. These flakes give up their water when exposed to a high temperature (Liebig; Liebig & Wöhler).

δ. *Nitrogen-nucleus.* $C^6N^3Br^3$?

Solid Bromide of Cyanogen?

1 pt. of anhydrous hydrocyanic acid forms with 3 pts. of bromine, a solid compound having the odour of mice, probably therefore corresponding to solid chloride of cyanogen (Serullas, *Ann. Chim. Phys.* 38, 374; also *Pogg.* 14, 446).

ε. *Nitrogen-nucleus.* $C^6N^3Cl^2H$.

Chlorhydride of Cyanogen. $C^6N^3Cl^2H$.

WURTZ (1847). *Compt. rend.* 24, 437.

Chlorhydrocyan, Chlorohydrure de Cyanogène, [*Prussek.*]

Concentrated hydrocyanic acid through which chlorine is passed, becomes heated after a while, acquires the odour of volatile chloride of cyanogen, and gives off the vapour of chlorohydride of cyanogen. If therefore the hydrocyanic acid be contained in a tubulated retort, through the tubulure of which chlorine gas is passed, and the neck of the retort be connected with a chloride of calcium tube, and then with a knee-shaped tube leading downwards into a long-necked flask surrounded with ice, the chlorhydride of cyanogen condenses in the flask, and may be freed from admixed hydrochloric and hydrocyanic acid, by agitating it with two or three times its bulk of cold water; it is then decanted from the water, and rectified in such a manner that the vapour may be compelled to pass through a tube containing chloride of calcium.

Transparent, colourless liquid, lighter than water; boils at 20°. The vapour has a powerful odour, irritates the bronchial tubes strongly, and excites a copious flow of tears.

The vapour burns with a violet flame. — Dry chlorine gas converts the compound completely into solid chloride of cyanogen:

$$C^6N^3HCl^2 + 2Cl = C^6N^3Cl^3 + HCl.$$

When therefore a few grammes of the liquid are introduced into a bottle filled with chlorine gas, the sides of the bottle become covered with radiating needles, and the viscid liquid at the bottom is ultimately converted into large crystals of solid chloride of cyanogen. — Chlorhydride of cyanogen is decomposed by mercuric oxide, with violent evolution of heat, into liquid chloride of cyanogen (p. 465), cyanide of mercury, and water:

$$C^6N^3HCl^2 + HgO = C^4N^2Cl^2 + C^2NHg + HO.$$

It may therefore be regarded as a compound of liquid chloride of cyanogen with hydrocyanic acid = $C^2NH,C^4N^2Cl^2 = 2CyCl,HCy$ (*Comp.* VIII, 144, where the analysis is given.)

The liquid dissolves perceptibly in water, forming a solution which gives a white precipitate with nitrate of silver (Wurtz).

ζ. *Nitrogen-nucleus.* $C^6N^3Cl^3$.

Solid Chloride of Cyanogen.

SERULLAS. *Ann. Chim. Phys.* 35, 291 and 337; abstr. *Pogg.* 11, 87. — *Ann. Chim. Phys.* 38, 370; also *Pogg.* 14, 443; also *N. Tr.* 18, 2, 131.

LIEBIG & WÖHLER. *Pogg.* 20, 369; also *Mag. Pharm.* 33, 137.

LIEBIG, *Pogg.* 34, 604.

Fixed chloride of Cyanogen, fixes Chlorcyan, festes Chlorcyan, Chlorure de Cyanogène solide, Perchlorure de Cyanogène. [Prussik.] — Discovered by Serullas in 1827, and regarded as bichloride of cyanogen, till its true composition was pointed out by Liebig.

Formation. — 1. Gaseous chloride of cyanogen changes spontaneously into the solid compound (Liebig). — Solid chloride of cyanogen is formed by the action of excess of chlorine in sunshine on anhydrous hydrocyanic acid, or on slightly moistened cyanide of mercury, which however yields other products at the same time (Serullas):

$$3C^2NH + 6Cl = C^6N^3Cl^3 + 3HCl.$$

If the quantity of hydrocyanic acid be twice or thrice as great as the chlorine is able to decompose, a viscid yellow liquid is produced; and with still more hydrocyanic acid, a hyacinth-coloured, nearly solid mass which when exposed to the open air, gives off hydrocyanic acid with a kind of ebullition till nothing is left but white solid chloride of cyanogen. By the admission of a larger quantity of chlorine gas also, the viscid liquid is completely converted into solid chloride of cyanogen (Serullas). — 3. When heated sulphocyanide of potassium is decomposed by dry chlorine gas, solid chloride of cyanogen, amounting to 4 or 5 per cent, passes over together with chloride of sulphur, and sublimes in needles (Liebig).

Preparation. 1. A bottle of 1 litre capacity is filled with dry chlorine gas; 0·82 grm. of hydrocyanic acid prepared by Gay-Lussac's method, introduced into it; and the closed bottle exposed to the sun for 1 to 3 days, whereupon the hydrocyanic acid evaporates, the chlorine gas is decolorized, and a transparent colourless liquid formed, which runs down the sides of the vessel, and soon solidifies in white crystals of solid chloride of cyanogen. The hydrochloric acid gas, together with any volatile chloride of cyanogen that may be present, is then blown out of the bottle with a pair of bellows; a small quantity of water and a few pieces of glass introduced, in order to detach the crystallized solid chloride of cyanogen from the sides of the vessel by agitation; the whole poured into a basin; the pieces of glass taken out; the solid chloride of cyanogen comminuted with a glass rod; repeatedly washed on a filter with a small quantity of cold water, till the liquid which runs away no longer forms a cloud with nitrate of silver (this wash-water, which contains hydrochloric acid, cyanuric acid, and a small quantity of chlorocyanic oil, may be used for the preparation of cyanuric acid, p. 450); the solid chloride of cyanogen pressed between bibulous paper, till it is converted into a dry white powder; and this powder purified by one or two distillations from a small retort, whence it passes, in the form of a transparent colourless liquid, into a receiver cooled with wet linen, and there solidifies.

2. When dry cyanogen gas is passed over heated sulphocyanide of potassium, solid chloride of cyanogen partly sublimes in needles, partly distils over dissolved in chloride of sulphur. — The needles are purified from adhering chloride of sulphur by a second sublimation in a vessel through which a continuous stream of chlorine gas is passed. — The chloride of sulphur which passes over, leaves when evaporated, an additional quantity of crystals of solid chloride of cyanogen, together with a yellow liquid having a high boiling point. From this residue, the

chloride of cyanogen is separated by sublimation in a stream of chlorine gas, the yellow liquid then remaining behind (Liebig).

Properties. Shining white needles (and laminæ: *Liebig*), of sp. gr. about 1·320, melting at 140° to a transparent, colourless liquid, and boiling at 190° (Serullas). Vapour-density 6·35 (Bineau, *Ann. Chim. Phys.* 68, 424). — Gives out, especially when heated, a pungent odour like that of chlorine, but at the same time strikingly resembling that of mice, and excites tears. Its taste is weak, in consequence of its small solubility, but is nevertheless similar to the odour. One grain dissolved in alcohol, and introduced into the alimentary canal of a rabbit, kills it instantly (Serullas).

		Liebig.	Serullas.		Vol.	Density.
6 C	36·0	19·54		C-vapour	6	2·4960
3 N	42·0	22·80		H-gas	3	2·9118
3 Cl	106·2	57·66	56·91 ... 74·35	Cl-gas	3	7·3629
$C^6N^3Cl^3$	184·2	100·00			2	12·7707
					1	6·3853

Decompositions. 1. Solid chloride of cyanogen dissolves in water without decomposition at first, but is afterwards resolved with it, slowly at ordinary temperatures, more quickly at a boiling heat, and instantly in presence of a fixed alkali, into hydrochloric and cyanuric acids (Serullas):

$$C^6N^3Cl^3 + 6HO = C^6N^3H^3O^6 + 3HCl.$$

100 pts. of solid chloride of cyanogen, heated for some time with water to 50° or 60°, gradually disappear, being dissolved in the form of hydrochloric and cyanuric acids; the solution evaporated to perfect dryness, leaves 70·69 pts. of dry cyanuric acid (Liebig). Calculation gives 70·08 pts. — Similarly, chloride of cyanogen boiled with ammonia, water, and alcohol, yields sal-ammoniac and cyanuric acid; but in the absence of alcohol, chlorocyanamide is produced. The same compound is formed, with slight evolution of heat, when dry ammoniacal gas is passed over pulverized chloride of cyanogen (Liebig). — 2. Solid chloride of cyanogen mixed with potassium is decomposed, with evolution of light and heat, yielding chloride and cyanide of potassium (Serullas).

$$C^6N^3Cl^3 + 6K = 3C^2NK + 3KCl.$$

Combinations. — Solid chloride of cyanogen is but very slightly soluble in *Water*. The highly poisonous action of this solution shows that, when first formed, it contains undecomposed chloride of cyanogen (Serullas).

It dissolves very readily in *Alcohol* and *Ether*, whence it is precipitated by water. Chloride of cyanogen dissolved in absolute alcohol remains unaltered; but in hydrated alcohol, it is converted in a short time, with violent evolution of heat, into vapours of hydrochloric acid, and cubes of cyanuric acid which settle at the bottom of the liquid (Liebig).

Compounds related to Solid Chloride of Cyanogen.

1. Liquid Chloride of Cyanogen. $C^4N^2Cl^2$?

WURTZ (1847). *Compt. rend.* 24, 438. — Further: *Ann. Pharm.* 79, 280.

Produced on bringing chlorhydride of cyanogen (hydrocyanate of chloride of cyanogen) with mercuric oxide (p. 463; also VIII, 142). To prevent the great rise of temperature which this action tends to produce, the mercuric oxide is mixed with recently fused and pulverized chloride of calcium; the mixture well cooled; the chlorhydride of cyanogen then added; and the product distilled some hours afterwards into a well-cooled receiver.

The colourless distillate is heavier than water; crystallizes at — 7° in long, transparent laminæ; boils at + 16°. [According to Wurtz's later investigations, the liquid crystallizes between — 5° and — 6°, and boils at + 15·5°]. Its vapour excites violent coughing and copious flow of tears. [For the analysis, see VIII, 143].

The vapour is not inflammable. — The liquid mixed with a small quantity of potash, and then with a larger quantity of nitric acid, gives off carbonic acid gas, and leaves chloride of potassium, which precipitates nitrate of silver, whereas the aqueous solution of the undecomposed compound remains clear when mixed therewith. Probably, chloride of potassium and cyanate of potash are first formed; and the latter, on addition of nitric acid, yields carbonic acid and ammonia:

$$C^4N^2Cl^2 + 4KO = 2KCl + 2C^2NKO^2.$$

The compound is perceptibly soluble in water (Wurtz).

2. Chlorocyanic Oil.

GAY-LUSSAC. *Ann. Chim.* 95, 200; also *Gilb.* 53, 168; also *Schw.* 16, 55.

SERULLAS. *Ann. Chim. Phys.* 35, 300. — 38, 391; also *Pogg.* 14, 443.

BOUIS. *Compt. rend.* 21, 226; also *J. pr. Chem.* 37, 278. — *N. Ann. Chim. Phys.* 20, 446; also *J. pr. Chem.* 42, 45.

Chlorocyan-öl; called *Acide chlorocyanique* by Gay-Lussac; *yellow liquid* or *yellow oil* by Serullas and Bouis. — Gay-Lussac, in 1815, first obtained this oil in the separate state, but did not accurately distinguish it from volatile chloride of cyanogen. Serullas pointed out the diversity of the two compounds, and endeavoured, as did afterwards Bouis, to ascertain its composition.

Formation. — By the action of chlorine on many cyanogen-compounds: *e.g.* of cyanogen gas and chlorine in sunshine (Gay-Lussac); in presence of moisture (Serullas); of anhydrous hydrocyanic acid and moist chlorine gas in sunshine (Gay-Lussac, Serullas); also when chlorine gas is passed through strong aqueous hydrocyanic acid, oily drops being deposited on the sides of the vessel (Gay-Lussac). — Also by the action of chlorine gas on dry cyanide of mercury in sunshine (Gay-Lussac). The action is complete in ten days; the oil is the only product, no chloride of cyanogen

being formed (Serullas). By the action of chlorine gas in sunshine on cyanide of mercury pulverized and suspended in water, or in the state of aqueous solution. In these decompositions of cyanide of mercury, the first products formed appear to be chloride of mercury and volatile chloride of cyanogen; but the latter is afterwards decomposed by the excess of chlorine and converted into the oil (Serullas). — Carbonic acid and volatile chloride of cyanogen are given off, and the water is found to contain in solution, hydrochloric acid, sal-ammoniac, and protochloride of mercury (Bouis). — The same yellow oil appears also to be formed where solid chloride of cyanogen is heated in a stream of chlorine (*comp.* Liebig, *Ann. Pharm.* 10, 42).

Preparation. A concentrated aqueous solution of 5 grms. cyanide of mercury is poured into a bottle of one litre capacity, filled with chlorine gas and exposed to the sun: in an hour or two, drops of oil are seen running down the sides, and in four hours, if the sunshine be strong, the action is complete. In diffused daylight, the decomposition goes on more slowly and yields less oil. The oil is mechanically separated from the water above it — a large quantity of volatile chloride of cyanogen then escaping — and drawn up into tubes under water (Serullas). — Bouis proceeds in the same manner, except that he prepares a solution of cyanide of mercury saturated at a boiling heat, and pours it while still hot into bottles filled with chlorine. The crystals of cyanide of mercury which form at first, soon dissolve, and are replaced by elongated crystals, the formation of which appears however to be merely accidental; afterwards the oily drops appear. The chlorine must be repeatedly renewed, till it no longer loses its colour. In the bright sunshine of summer, the saturation of the liquid with chlorine is completed in two hours; in winter it takes two or three weeks. Four parts of cyanide of mercury yield 1 pt. of the oil (Bouis).

Properties. Yellow oil, heavier than water. Has a very pungent odour, like that of chloride of cyanogen, but with a peculiar aromatic character, causing a copious flow of tears and coughing. It is not nearly so poisonous as chloride of cyanogen, a tolerably strong dose killing rabbits only after several hours. When recently prepared, it does not redden litmus or precipitate nitrate of silver (Serullas). Its boiling point is at least as high as that of oil of vitriol (Liebig). It makes grease-spots on paper, which are dissipated by heat. Has a very caustic taste (Bouis)

Dried over chloride of calcium after thorough washing.				Bouis.
12 C	72·0	11·54		10·67
4 N	56·0	8·98		8·38
14 Cl	495·6	79·48		78·63
$C^{12}N^4Cl^{14}$	623·6	100·00		97·68

May be regarded as $C^8N^4Cl^8,C^4Cl^8$. Its formation is explained in the following manner: $8C^2N$ with 16Cl form $2C^8N^4Cl^8$; one atom of this $C^8N^4Cl^8$ remains undecomposed; the other is decomposed by the water, yielding sesquichloride of carbon (which unites, *in the nascent state*, with the undecomposed portion of $C^8N^4Cl^8$, forming chlorocyanic oil) and sal-ammoniac, carbonic acid, and nitrogen, according to the following equation (Bouis):

$$C^8N^4Cl^8 + 8HO = C^4Cl^4 + 2NH^4Cl + 4CO^2 + 2N.$$
$$2 \quad \text{II} \quad 2$$

[According to Gay-Lussac and Serullas, however, the chlorocyanic oil is likewise formed by the action of dry chlorine on dry cyanide of mercury]. — Serullas regards chlorocyanic oil as a mixture of chloride of cyanogen, which might be an intermediate liquid modification [probably the compound described on p. 467?] with protochloride of carbon and chloride of nitrogen. The conclusion that the presence of chloride of nitrogen in the oil should impart detonating properties to it, appears to be unfounded: for chlorocyanic oil, to which chloride of nitrogen has actually been added, gives off gas in contact with phosphorus more rapidly than the pure oil, but does not explode (Serullas).

According to Bouis, on the contrary, chlorocyanic oil explodes by the mere action of heat (*vid. inf.*).

Decompositions. — Chlorocyanic oil, when kept, either in the moist or in the dry state, becomes paler in colour, and deposits crystals of sesquichloride of carbon (Bouis). When very cautiously distilled (on account of its great tendency to explode) in a water-bath, the temperature of which is gradually raised, it boils at a moderate heat, giving off carbonic acid and nitrogen gases, and yields a colourless distillate, from which sesquichloride of carbon crystallizes on cooling. If the distillation be repeated a few times (whereby no more gas is evolved), collecting only the more volatile portion of each distillate, and separating the sesquichloride of carbon which crystallizes out on cooling, *a peculiar distillate* is obtained (Bouis).

This *peculiar transparent and colourless distillate* is heavier than water; begins to boil at 85°, the boiling point continually rising; has a very irritating odour, and caustic taste; and reddens litmus strongly. After drying over chloride of calcium, it contains 12·09 p.c. C, 5·00 N and 81·26 Cl (loss 1·65), and is therefore $C^{20}N^4Cl^{22} = C^8N^4Cl^4 + 3C^4Cl^6$. It burns with a red flame, green at the edges. With sal-ammoniac it yields sesquichloride of carbon and other products. It is insoluble in water, but dissolves readily in alcohol, and still more in ether (Bouis). — The formation of this transparent, colourless distillate from chlorocyanic oil, may be explained as follows: The compound $C^8N^4Cl^8$, which may be supposed to exist, together with C^4Cl^6, in chlorocyanic oil, is resolved into nitrogen, sesquichloride of carbon, and $C^8N^4Cl^4$, according to the following equation:

$$2C^8N^4Cl^8 = 4N + 2C^4Cl^6 + C^8N^4Cl^4.$$

This $C^8N^4Cl^4$ then unites with $3C^4Cl^6$, and forms the colourless distillate, or, which comes to the same thing:

$$2C^{12}N^4Cl^{14} = 4N + C^4Cl^6 + C^{20}N^4Cl^{22} \text{ (Bouis)}.$$

When chlorocyanic oil is suddenly heated, it detonates violently; *e. g.* when a few drops of the oil contained in a glass tube are plunged into water at 85°; or when the neck of a glass bulb containing the oil is sealed (Bouis). If, however, the chlorocyanic oil has been previously brought to the boiling point by very gradual heating in the water-bath, and the boiling then kept up for a few minutes, all danger of explosion is over, and the distillation may then be continued over the open fire (Bouis). — [This circumstance seems to indicate the presence of chloride of nitrogen, that compound volatilizing at the beginning of the distillation].

When chlorocyanic oil is distilled over a mixture of chloride of

calcium and carbonate of lime, a very pungent, acid, colourless liquid first passes over, with considerable evolution of gas; then a crystalline sublimate is obtained, and charcoal remains behind. If the colourless distillate thus obtained be several times redistilled over fresh quantities of chloride of calcium and carbonate of lime, no more gas is obtained, but white crystals of sesquichloride of carbon again separate out; and the distillate, — although the carbonate of lime each time retains a portion of chlorine, — becomes continually more acid and more pungent in odour, and behaves like a mixture of protochloride of carbon and hydrochloric acid (Serullas).

Chlorocyanic oil kept under water, gradually loses its colour, and continues, even for a year, to give off bubbles of a mixture of 3 vol. nitrogen, and 1 vol. carbonic acid, and deposits white flakes or crystals of sesquichloride of carbon, while hydrochloric acid dissolves in the water. At 100°, this decomposition takes place much more quickly; but the products, and the proportion of the carbonic acid and nitrogen, remain the same (Serullas). [The explanation which Serullas gives of this reaction, is not satisfactory].

Chlorocyanic oil immersed in water continually gives off nitrogen and carbonic acid gas. The oil, after being well washed with water, does not redden litmus at first; but in a few seconds becomes strongly acid, from the continuous formation of hydrochloric acid. When immersed in water in a bottle filled with chlorine, and exposed to the sun, it gives off nitrogen and carbonic acid, and deposits crystals of sesquichloride of carbon (Bouis).

Chlorocyanic oil, when set on fire, burns without explosion, with a red, slightly smoky flame, and leaves no residue. It may be analyzed with oxide of copper, without risk of explosion (Bouis).

Chlorine does not decompose it (Bouis).

Cold concentrated nitric acid does not act upon chlorocyanic oil at first; but when gently heated, it boils and gives off streams of gas which break the vessel. If the cold acid be allowed to act quietly for the first two hours, and the mixture afterwards very slowly heated in a retort, it gives off carbonic acid gas, nitrogen, yellowish nitrous vapours having a powerful odour, and yields a distillate consisting of two layers, the upper of which is nitric acid, the lower an oily liquid. If the latter be repeatedly distilled,—an operation which may be performed over the open fire,—collecting each time only the first portions, and separating them from the sesquichloride of carbon, which passes over with them or crystallizes from the distillate; and the liquid washed with water as soon as the crystals cease to appear on further distillation, then dried [over chloride of calcium], and again partially distilled, the *liquid* $C^{12}N^4Cl^{14}O^4$ is obtained.

This *liquid*, $C^{12}N^4Cl^{14}O^4$, is transparent, colourless, heavier than water; very volatile; has a more pungent and irritating odour than chlorocyanic oil; makes oily spots on paper, which disappear when heated; has an extremely sour and caustic taste; and produces fumes in the air. It contains 10·18 p.c. C, 8·53 N, 75·80 Cl and 5·49 O. It burns with a reddish flame, and is insoluble in water, but dissolves in alcohol and ether (Bouis).

When dry ammoniacal gas is slowly passed over chlorcyanic oil, the oil becomes turbid and hot, and solidifies in a white mass, which afterwards turns red and becomes still hotter; the sides of the vessel also become covered with a red substance containing white crystals. The

mass dissolves very sparingly in water, and partially in alcohol and ether, leaving a red powder; the solution reddens litmus slightly, forms a precipitate with nitrate of silver; and when evaporated, deposits crystals of sesquichloride of carbon. — Aqueous ammonia in contact with chlorocyanic oil, gives off a gas having a strong, penetrating odour, and deposits at first a white mass of sal-ammoniac; then, after longer standing, a yellow crystalline mass, which afterwards changes to brick-red. This mass is likewise insoluble in water, and dissolves but partially in alcohol and ether. The alcoholic solution diluted with water deposits crystals of sesquichloride of carbon. The brick-red body insoluble in alcohol dissolves in nitric acid, and likewise, with evolution of ammonia, in potash. Heated with potassium, it unites with that body, with evolution of light and heat, and forms a melting mass which, on continued exposure to heat, assumes a greenish colour. After cooling, it dissolves in water, leaving only a small quantity of a white gelatinous substance soluble in acids (Bouis).

Chlorocyanic oil and potassium may be kneaded together at ordinary temperatures; but even a slight elevation of temperature causes violent detonation; similarly, if the oil be gently heated with potassium over mercury, then a small quantity of hydrochloric acid passed up, and the mixture slightly agitated. The oil dropped upon potassium gently heated in a capsule, burns gently with greenish white flame; if fresh oil be then added with a glass rod, repeated detonations take place as often as pressure is exerted, accompanied by a pungent odour of chloride of cyanogen, and a white cloud, probably consisting of chloride of potassium. The residual mass containing potassium, forms, when dissolved in water, a precipitate of prussian blue with iron salts and hydrochloric acid. The colourless liquid obtained by distillation over chloride of calcium and carbonate of lime, though it probably no longer contains chloride of nitrogen, likewise forms with potassium a mass which detonates when heated (Serullas). Chlorocyanic oil strongly pressed in contact with potassium, also detonates violently, and with a red flame (Bouis).

Combinations. Chlorocyanic oil is insoluble in water, but dissolves readily in *Alcohol*, from which it is precipitated by water, in the form of a colourless, and partly solid substance, having a camphorous but at the same time pungent odour (Serullas). — According to Bouis, the oil is precipitated by water unchanged, and with milky turbidity. — It is likewise soluble in ether (Bouis).

η. *Nitrogen-nucleus* $C^6N^3AdH^3$?

Product obtained from Urea. $C^6N^4H^4O^4 = C^6N^3AdH^3,O^4$?

Wöhler & Liebig (1845). *Ann. Pharm.* 54, 371.
Liebig. *Ann. Pharm.* 57, 114; — 58, 249 & 255.
Gerhardt. *N. J. Pharm.* 8, 388.
Laurent & Gerhardt. *Compt. rend.* 22, 456. — *N. Ann. Chim. Phys.* 19, 93.

Formation (VII, 366).

Preparation. When urea is slowly heated in a retort up to a certain temperature, there remains a mixture of this product with a varying

quantity of cyanuric acid, which may be removed by boiling with water (Wöhler & Liebig). — Laurent & Gerhardt heat the urea in a capsule to a temperature above its melting point, till it boils, gives off carbonic acid and carbonate of ammonia, and is converted, first into a paste, then into a dry mass, which they wash with water. By this process, 2 pts. of urea yield about 1 pt. of residue. If part of it has been converted by too high a temperature into mellone, the product is to be treated with boiling ammonia or weak potash, filtered from the mellone, and the product precipitated by nitric acid.

Properties. Snow-white, chalky powder (Wöhler & Liebig).

	Dried at 100°.			Laurent & Gerhardt.
6 C	36	....	28·12	..... 27·9
4 N	56	....	43·75	
4 H	4	....	3·13	..... 3·2
4 O	32	....	25·00	
$C^6N^4H^4O^4$	128	....	100·00	

According to the formula $C^6N^2Ad^2O^2,O^2$, the compound should be an aldide; according to the formula, $C^6N^3AdH^2,O^4$, it is an acid, — and this latter view is in accordance with many of its relations to salifiable bases, as also with its resemblance to hydrosulphomellonic acid (p. 472). — Gerhardt & Laurent regard this residue as identical with Liebig's ammelide.

The residue yields yellow mellone when heated (Wöhler & Liebig). It is resolved by heat, without yielding a trace of water, into ammonia and cyanic acid which volatilize, cyanuric acid which sublimes, and mellone (Laurent & Gerhardt):

$$6C^6N^4H^4O^4 = 3NH^3 + 3C^2NHO^2 + 3C^6N^3H^3O^6 + C^{12}N^9H^3.$$

2. By boiling with acids or alkalis, it is converted into ammonia and cyanuric acid (Wöhler & Liebig):

$$C^6N^4H^4O^4 + 2HO = C^6N^3H^3O^6 + NH^3.$$

Combinations. The residue is insoluble in water; easily soluble in acids and alkalis; and may be precipitated therefrom by neutralization (Wöhler & Liebig).

From the ammoniacal solution, ammonia throws down a compound which gives off nearly all its ammonia on exposure to the air. The precipitate thrown down by alcohol from the solution in potash, contains only 6·9 p.c. potash, which may be almost wholly removed by repeated washing with water (Laurent & Gerhardt).

The saturated solution of the urea-residue in boiling ammonia, forms with aqueous nitrate of silver a precipitate, which, after drying at 100°, contains 46 p.c. nitrate of silver; it is therefore $C^6N^4H^3AgO^4$, and is doubtless identical with the compound of ammelide and silver-oxide (p. 477) obtained by Knapp (Laurent & Gerhardt).

Hydrosulphomellonic Acid. $C^6N^4H^4S^4 = C^6N^3AdH^3,S^4$.

JAMIESON. (1846). *Ann. Pharm.* 59, 340.

Hydrothiomellon, Hydroschwefelmellonsäure, Schwefelmellonwasserstoffsäure, Acid hydrosulfo-mellonique, Ammelide sulfuré.

Formation (VIII, 110, 5).

Preparation. A tolerably concentrated aqueous solution of hydrosulphate of potassium is saturated with pseudosulphocyanogen, the liquid being at last heated to the boiling point; the solution then filtered; kept at a boiling heat for ten or twelve hours; and neutralized when cold with acetic acid, which throws down a copious precipitate of hydrosulphomellonic acid mixed with sulphur. Part of it remains, however, dissolved in the liquid, and may be obtained by evaporation. — The well-washed precipitate is treated with cold ammonia, which leaves nearly all the sulphur undissolved; the filtrate placed in a warm situation till nearly every trace of sulphide of ammonium has disappeared; boiled with animal charcoal till a sample treated with a mineral acid yields a perfectly white precipitate; and the entire liquid, after filtration, precipitated by an acid.

Properties. Hydrosulphomellonic acid crystallizes from boiling water in delicate white needles; from a salt it is precipitated as a white powder. It is tasteless. Its aqueous solution reddens litmus.

				Jamieson.
6 C	36	....	22·50	..... 22·56
4 N	56	....	35·00	..... 35·08
4 H	4	....	2·50	..... 2·68
4 S	64	....	40·00	..... 39·94
$C^6N^4H^4S^4$	160	....	100·00	..... 100·26

The urea-residue (p. 470), in which O is replaced by S. (Gerhardt & Laurent, *N. J. Pharm.* 11, 229, and *N. Ann. Chim. Phys.* 20, 118).

Decompositions. 1. Hydrosulphomellonic acid heated to between 140° and 150°, gives off sulphuretted hydrogen, and leaves mellone — 2. Hot nitric acid converts it into cyanuric acid. — 3. When heated with sulphuric or hydrochloric acid, it gives off sulphuretted hydrogen, and yields cyanuric acid. Ammonia must be formed at the same time, according to the following equation (Laurent & Gerhardt):

$$C^6N^4H^4S^4 + 6HO = C^6N^3H^3O^6 + 4HS + NH^3.$$

Combinations. Hydrosulphomellonic acid is nearly insoluble in cold water, and dissolves but very sparingly in boiling water, crystallizing out again on cooling.

It unites with salifiable bases, giving out 1 At. water.

Sulphomellonide of Potassium. — Potash-ley saturated while hot with hydrosulphomellonic acid and filtered hot, yields on cooling, colourless prisms belonging to the right prismatic system, and having a vitreous lustre. These crystals give off a large quantity of water at 100°, and

the rest at 120°, the whole quantity amounting to 11·73 p. c. (3 At.) The compound, when further heated, gives off sulphide of ammonium and hydrocyanic acid, and leaves a residue whose aqueous solution forms a gelatinous precipitate with hydrochloric acid. — Sulphomellonide of potassium dissolves very readily in water and alcohol; chlorine gas passed through the aqueous solution throws down a white substance, probably $= C^6N^4H^3S^4$.

	Dried at 100°.			Jamieson.
6 C	36·0	....	18·16	
4 N	56·0	....	28·25	
3 H	3·0	....	1·52	
K	39·2	....	19·78	..... 19·70
4 S	64·0	....	32·29	
$C^6N^4H^3KS^4$	198·2	....	100·00	

Sulphomellonide of Sodium. — Prepared in a similar manner. Broad, translucent tables having a fatty lustre, — or from a quickly cooled solution: nacreous laminæ, which give off 12·89 per cent (3 At.) water at 120°, leaving the anhydrous compound ($= C^6N^4H^3NaS^4$) which contains 12·66 p.c. sodium.

Sulphomellonide of Barium. — Formed by boiling hydrosulphomellonic acid with water and carbonate of baryta, till the mixture no longer effervesces, then filtering, and evaporating to the crystallizing point. Colourless needless with a diamond lustre, which give off 16,62 p.c. (5 At.) water at 120°.

	Dried at 120°.			Jamieson.
6 C	36·0	....	15·82	..... 16·04
4 N	56·0	....	24·60	..... 23·90
3 H	3·0	....	1·31	..... 1·43
Ba	68·6	....	30·15	..... 39·45
4 S	64·0	....	28·12	..... 28·21
$C^6N^4H^3BaS^4$	227·6	....	100·00	..... 100·03

Sulphomellonide of Strontium. — Prepared in a similar manner. Large, translucent tables belonging to the square prismatic system and having a waxy lustre; they give off 14·95 p.c. (4 At.) water of crystallization at 120°, leaving the anhydrous compound which contains 20·80 per cent of strontium.

Sulphomellonide of Calcium. — Prepared in a similar manner. Colourless needles with a glassy lustre, belonging to the doubly oblique prismatic system, and resembling those of axinite. At 120°, they give off 11·21 p.c. (2 At.) water of crystallization, and leave the anhydrous salt, containing 11·23 per cent. of calcium.

Sulphomellonide of Magnesium. — Prepared in a similar manner. Small needles, which have a glassy lustre, dissolve readily in water, and give off 23·93 p.c. (6 At.) water at 120°, leaving a residue which contains 7·24 p.c. of magnesium.

Sulphomellonide of Silver. — A solution of hydrosulphomellonic acid in aqueous ammonia, forms with nitrate of silver, thick white flakes, which

are perfectly insoluble in water and do not blacken on exposure to light or suffer decomposition at 100° (Jamieson).

	Dried at 100°.		Jamieson.
6 C	36	13·49	13·55
4 N	56	20·97	21·07
3 H	3	1·12	1·31
Ag	108	40·45	40·67
4 S	64	23·97	24·01
$C^6N^4H^2AgS^4$	267	100·00	100·61

θ. Nitrogen-nucleus. $C^6N^3Ad^2H$.

Ammeline. $C^6N^3H^5O^2 = C^6N^3Ad^2H,O^2$?

Liebig (1834). *Ann. Pharm.* 10, 24; also *Pogg.* 34, 592.
Knapp. *Ann. Pharm.* 21, 243 and 255.
Völckel. *Pogg.* 62, 90.

Formation. 1. By boiling melam with hydrochloric acid or dilute sulphuric acid, or with solution of potash (in the last case together with melamine. (Liebig). — 2. By boiling melamine with dilute nitric acid (Knapp).

Preparation. After the melamine has crystallized out from a solution of melam in boiling potash-ley, the ammeline may be thrown down in the form of a thick white precipitate, by acetic acid, sal-ammoniac, or carbonate of ammonia. It is washed with water; dissolved in dilute nitric acid; the nitrate of ammeline crystallized out and dissolved in water containing a little nitric acid; the ammeline precipitated therefrom by ammonia, or carbonate of potash; and the precipitate washed and dried (Liebig). Völckel dissolves his poliene in strong boiling hydrochloric acid, and precipitates ammeline from the solution by ammonia.

Properties. Snow-white, bulky powder, having a silky lustre when precipitated by ammonia (Liebig).

		Liebig.	Knapp.	Völckel.
6 C	36	28·46	28·04	28·28
5 N	70	54·94	54·12	55·00
5 H	5	3·97	3·83	4·00
2 O	16	12·63	14·01	12·72
$C^6N^3H^5O^2$	127	100·00	100·00	100·00

According to Liebig, ammeline is $3Cy,2NHO^2,3H$. [If we were to assign to it the formula $C^6N^3Ad^2H,O^2$, it would be regarded as an amidated aldide, which, like urea, possesses weak basic properties; the formula $C^6N^4AdHO^2,H^2$ would represent it as an alkaloïd, in the nucleus of which, 6 C would be united, not with 6 At. but with 8 At. of other substances; according to the formula C^6N^4AdH,H^2O^2, it would be an alcohol.]

Decompositions. 1. Ammeline when heated yields ammonia and a crystalline sublimate, and leaves yellow mellone (Liebig). According to Laurent & Gerhardt, it is thereby resolved into ammonia, cyanuric acid,

and mellone; but the cyanuric acid volatilizes in the form of cyanic acid. They represent the decomposition by the following equation:

$$3C^6N^5H^5O^2 = 3NH^3 + C^6N^3H^3O^6 + C^{12}N^9H^3.$$

2. By solution in oil of vitriol, it is resolved into ammonia and ammelide, which latter may be precipitated by alcohol (Liebig):

$$2C^6N^5H^5O^2 + 2HO = C^{12}N^9H^9O^6 + NH^3.$$

(Or, according to Laurent & Gerhardt, who regard ammelide as $C^6N^4H^4O^4$:

$$C^6N^5H^5O^2 + 2HO = C^6N^4H^4O^4 + NH^3).$$

Ammeline is also resolved into ammonia and ammelide by continued boiling with dilute nitric acid, the ammelide being then, by boiling for 14 hours longer, completely resolved into ammonia and cyanuric acid (Knapp). — 3. Dry ammeline fused with hydrate of potash, intumesces strongly, and gives off ammonia and water, while pure cyanate of potash remains behind (Liebig):

$$C^6N^5H^5O^4 + 4HO = 3C^2NHO^2 + 2NH^3.$$

Combinations. Ammeline is insoluble in water.

With strong acids, ammeline behaves like a weak base, but does not dissolve in acetic acid, and is incapable of decomposing ammoniacal salts. With most acids it forms crystallizable salts, which are partially decomposed by water, ammeline being left undissolved in the form of a white powder, and an acid solution formed, which gives a white precipitate with alkaline carbonates (Liebig).

Nitrate of Ammeline. — A solution of ammeline in dilute nitric acid yields by evaporation, long, transparent, colourless, square prisms, which have a high lustre and refract light strongly. These crystals heated to the point at which the mass, after becoming pasty, again solidifies, are resolved into nitric acid, nitrous oxide, and water (products of decomposition of the nitrate of ammonia which is at first formed) and a residue of ammelide:

$$2C^6N^6H^6O^8 = C^{12}N^9H^9O^6 + NH^3 + 2NO^5.$$

Water decomposes these crystals into free ammeline and an acid solution; from their saturated solution in aqueous nitric acid, the addition of more water throws down part of the ammeline (Liebig).

	Crystallized.			Liebig.
6 C	36	....	18·95	..... 19·02
6 N	84	....	44·21	..... 44·05
6 H	6	....	3·16	..... 3·20
8 O	64	....	33·68	..... 33·73
$C^6N^5H^5O^2,HO,NO^5$	190	....	100·00	..... 100·00

Ammeline dissolves in aqueous *Potash*, and is precipitated from the solution by acetic acid, sal-ammoniac, and carbonate of ammonia.

Ammeline with Silver-oxide. — The solution of ammeline in strong ammonia forms with nitrate of silver, a white precipitate which contains 46·4 p. c. silver, and is therefore $C^6N^5H^4AgO^2$ (Laurent & Gerhardt).

Nitrate of Silver and Ammeline. — Nitrate of ammeline forms with nitrate of silver, a white crystalline precipitate which does not give off water when heated (Liebig).

			Liebig.
6 C	36	12·12	12·70
6 N	84	28·28	29·42
5 H	5	1·68	1·77
AgO	116	39·06	38·13
7 O	56	18·86	17·98
$C^6N^5H^5O^2,AgO,NO^5$	297	100·00	100·00

Ammeline does not dissolve in alcohol or in ether (Liebig).

Ammelide. $C^{12}N^9H^9O^6 = C^6N^3Ad^2H,O^2 + C^6N^3AdH^2.O^4$?

Liebig (1834). *Ann. Pharm.* 10, 30; also *Pogg.* 34, 597. — *Ann. Pharm.* 58, 249.
Knapp. *Ann. Pharm.* 21, 244.

Formation. By treating melam, melamine, or ammeline with sulphuric or nitric acid (Liebig, Knapp).

Preparation. Melam or ammeline is dissolved in oil of vitriol, or melamine is dissolved in boiling concentrated nitric acid; the ammelide precipitated from the solution by alcohol and carbonate of potash; and the dense, white precipitate thoroughly washed with water (Liebig). — 2. Nitric acid of sp. gr. 1·49, very slightly heated, is saturated with melam; the solution left to cool, whereupon it solidifies in consequence of the separation of the ammelide; the latter washed with water; dissolved in [nitric acid to free it from admixed ammeline and cyanuric acid; precipitated therefrom by excess of ammonia, which holds the cyanuric acid in solution; the precipitate redissolved in nitric acid; reprecipitated by a slight excess of potash; the precipitate, which obstinately retains potash, diffused in water containing a small quantity of sulphuric acid, whereby it is freed from potash and ammeline; and the ammelide thus purified washed with water. (Knapp). — 3. Nitrate of ammeline is heated, till the mass, which at first becomes pasty, again solidifies (Liebig). Knapp dissolves this residue in sulphuric acid, precipitates by alcohol, and washes the precipitate.

Properties. White powder, which has no action upon vegetable colours (Liebig).

			Liebig.	Knapp.
12 C	72	28·24	27·54	28·06
9 N	126	49·41	47·84	48·76
9 H	9	3·53	3·61	3·55
6 O	48	18·82	21·01	19·63
$C^{12}N^9H^9O^6$	255	100·00	100·00	100·00

According to Liebig, ammelide is $6Cy + 3NHO^2 + 6N$. [May be regarded as ammeline + urea-product (p. 470) = $C^6N^5HO^2 + C^6N^4H^4O^4$, or as cyanurate of melamine: $C^{12}N^9H^9O^6 = C^6N^6H^6,C^6N^3H^3O^6$]. — Laurent & Gerhardt (*Compt. rend.*

18, 156; 22, 456, regard ammelide as identical with the above-mentioned urea-product, but without having analyzed it.

Decompositions. 1. Ammelide boiled for several hours with dilute phosphoric, sulphuric, hydrochloric, or nitric acid, till the liquid is no longer precipitated by ammonia, is resolved into ammonia and cyanuric acid (Knapp):

$$C^{12}N^9H^9O^6 + 6HO = 2C^6N^3H^3O^6 + 3NH^3.$$

The cyanuric acid obtained by the use of nitric acid amounts to between 88 and 97 pts. from 100 pts. of ammelide. Calculation (255 : 2 . 129 = 100 : 101) requires 101 pts. (Knapp). 2. Ammelide dissolved in a tenfold quantity of dilute potash, is in a similar manner converted by an hour's boiling, into cyanurate of potash, a large quantity of ammonia being at the same time evolved (Knapp). — 3. Ammelide fused with hydrate of potash yields cyanate of potash, with evolution of ammonia (Liebig):

$$C^{12}N^9H^9O^6 + 6KO = 6C^2NKO^2 + 3NH^3.$$

Combinations. Ammelide is insoluble in water (Liebig).

Ammelide dissolves in the stronger *Acids*, but without forming characteristic salts (Liebig). It dissolves readily in sulphuric, hydrochloric or nitric acid, and is precipitated therefrom by ammonia or carbonate of potash (Knapp).

The solution in *sulphuric* or *hydrochloric acid* saturated while hot, does not yield crystals on cooling (Knapp); the *nitric acid* solution yields crystals, from which however the whole of the acid may be extracted by water or alcohol (Liebig).

Ammelide dissolves very sparingly in *Ammonia*, but very easily in *Potash;* from the potash-solution saturated while hot, it is deposited on cooling, unchanged and in white crusts (Knapp).

It does not appear possible to form compounds of ammeline with baryta, oxide of lead, or oxide of copper (Knapp).

Ammelide with Silver-oxide. — Obtained by diluting the warm solution of ammelide in nitric acid with such a quanity of water, that the mixture shall yield no deposit on cooling; mixing it at a moderate heat with excess of nitrate of silver; and cautiously adding ammonia to the clear liquid, as long as a white curdy precipitate continues to form: this precipitate must then be washed with water in the dark. — The white precipitate is blackened by light while in the moist state; it is very hygroscopic, and dissolves readily in nitric acid and in ammonia (Knapp).

	Dried at 100°.		Knapp.
12 C	72	15·35	15·47
9 N	126	26·86	26·87
7 H	7	1·49	1·40
2 Ag	216	46·06	45·90
6 O	48	10·24	10·36
$C^{12}N^9H^7Ag^2O^6$	469	100·00	100·00

Nitrate of Silver and Ammelide. When the above-mentioned mixture of aqueous nitrate of ammelide and nitrate of silver is left to cool without addition of ammonia, it yields yellowish crystals. A solution of the compound of ammelide and silver-oxide in strong nitric acid, also yields transparent, colourless laminæ on evaporation. — The crystals heated in a

tube give off a large quantity of nitric acid, then cyanic acid, and leave metallic silver. In water they become opaque, and dissolve for the most part, leaving however a few flakes of ammelide. By repeated solution in water and evaporation, the compound is in the end completely resolved into nitrate and cyanurate of silver (Knapp). [According to what equation ?]

	Crystallized.		Knapp.
12 C	72	12·10	11·46
11 N	154	25·89	24·31
9 N	9	1·51	1·56
2 Ag	216	36·30	37·90
18 O	144	24·20	24·77
$C^{12}N^9H^9Ag^2O^6,2AgO,2NO^5$	595	100·00	100·00

Ammelide does not dissolve in acetic acid, alcohol, or ether (Knapp).

1. *Nitrogen-nucleus.* $C^6N^3Ad^2Cl$.

Chlorocyanamide. $C^6N^3H^4Cl = C^6N^3Ad^2Cl$.

Liebig. *Pogg.* 34, 609; also *Ann. Pharm.* 10, 43. — *Ann. Pharm.* 58, 249.
Bineau. *Ann. Chim. Phys.* 70, 254.
Laurent & Gerhardt. *Compt. rend.* 22, 455. — *N. Ann. Chim. Phys.* 19, 90, and 22, 98.

Cyanamid, Parachlorcyan-Ammoniak, Chlorocyanamid, Parachlorocyanate d'Ammoniaque. — Discovered by Liebig in 1834.

Formation. Gaseous or aqueous ammonia in contact with solid chloride of cyanogen forms, with slight evolution of heat, chlorocyanamide and sal-ammoniac (Liebig).

$$C^6N^3Cl^3 + 4NH^3 = C^6N^5H^4Cl + 2NH^4Cl \text{ (Laurent \& Gerhardt).}$$

Preparation. Ammoniacal gas is passed to saturation over finely pulverized solid chloride of cyanogen, which is heated towards the end of the reaction,—or the solid chloride of cyanogen is heated with aqueous ammonia,—and in both cases, the resulting sal-ammoniac is extracted by washing with cold water (Liebig).

Properties. Dull white or yellowish white powder, which cannot be volatilized without decomposition.

			Laur. & Gerh.	Liebig.
6 C	36·0	24·76	24·9	27·98
5 N	70·0	48·14		
4 H	4·0	2·75	2·7	3·23
Cl	35·4	24·35	24·8	
$C^6N^5H^4Cl$	145·4	100·00		

Chlorocyanamide when burnt yields 6 vol. carbonic acid gas to nearly 5 vol. nitrogen (Liebig).

Decompositions. 1. Chlorocyanamide heated only to 120°—130°, yields a sublimate consisting of shining, inodorous crystals, and at a higher temperature is resolved into a crystalline sublimate and a residue of lemon-yellow mellone (Liebig). The products of this decomposition are hydrochloric acid, sal-ammoniac, and mellone (Laurent & Gerhardt):

$$2C^6N^5H^4Cl = HCl + NH^4Cl + C^{12}N^9H^3.$$

2. It dissolves sparingly in aqueous potash, with evolution of ammonia; the solution saturated with acetic acid, yields no crystals of monocyanurate of potash, but white flakes (Liebig). The solution obtained by heating chlorocyanamide with potash-ley contains chloride of potassium and a compound of ammeline with potash (Laurent & Gerhardt):

$$C^6N^5H^4Cl + HO + KO = KCl + C^6N^5H^5O^2.$$

Hydrochloric acid added to the solution, throws down the ammeline as a bulky white precipitate; when precipitated by acetic acid, the ammeline carries a certain quantity of potash down with it. Chlorocyanamide may likewise be immediately converted into ammelide by treating it with strong solution of potash (Laurent & Gerhardt).

Combinations. Chlorocyanamide dissolves sparingly in hot water, and separates in white flakes on cooling (Liebig).

Bineau examined the mixture of chlorocyanamide and sal-ammoniac obtained by the action of ammoniacal gas on solid chloride of cyanogen—which mixture he regards as $4NH^3,C^6N^3Cl^3$ — without removing the sal-ammoniac by water. This mixture is white, inodorous, without distinct taste [excepting, probably, that of sal-ammoniac?], and permanent in the air. Heated over the flame of a spirit-lamp, it does not melt, but evolves hydrochloric acid gas, and towards the end a small quantity of ammonia; yields a sublimate of sal-ammoniac, and a white, fusible, and decomposible substance, and leaves mellone. Cold nitric acid converts it in a few hours into crystallized cyanuric acid. Oil of vitriol dissolves it rapidly, with evolution of hydrochloric acid gas. Aqueous hydrochloric acid has no action upon it. — Potash-ley dissolves it, with evolution of ammonia. — Water dissolves scarcely any of it, but acquires the power of forming a cloud with solution of silver (Bineau).

κ. *Nitrogen-nucleus.* $C^6N^4Ad^2$.

Melamine. $C^6N^6H^6 = C^6N^4Ad^2,H^2$?

Liebig (1834). *Ann. Pharm.* 10, 18; 26, 187.

Formation. By boiling melam with aqueous potash (p. 484, 6).

Preparation. Melam prepared by heating 8 pts. of sulphocyanide of potassium and 16 pts. of sal-ammoniac, and well washed, is mixed with a solution of 1 pt. hydrate of potash in 24 to 32 pts. of water, and boiled or nearly boiled, — the water as it evaporates being replaced by a solution of potash of equal strength, — till the melam is completely dissolved, and forms a clear solution; the filtrate is then evaporated at a gentle heat, till it deposits shining laminæ; then slowly cooled to the

crystallizing point; the crystals washed several times with cold water; and purified by recrystallization from hot water (Liebig).

Properties. Tolerably large, colourless rhombic octohedrons. *Fig.* 41, $a : a' = 75° 6'$; $a : a$ backwards $= 115° 4'$ (nearly). Cleavage parallel to t (*Fig.* 43). The crystals are permanent in the air; decrepitate when heated; and melt to a transparent liquid, which solidifies in a crystalline mass on cooling. Cannot be sublimed. Has no action on vegetable colours (Liebig).

	Crystallized.			Liebig.	Varrentr. & Will.
6 C	36	....	28·57	28·74	
6 N	84	....	66·67	66·67	66·22
6 H	6	....	4·76	4·83	
$C^6N^6H^6$	126	....	100·00	100·24	

Liebig gives the formula $Cy^3,3NH,3H$. [The formula $C^6N^4Ad^2,H^2$, is in accordance with the assumption (VII, 186), that the alkaloïds contain 2H, outside a itrogen-nucleus].

Decompositions. 1. Melamine heated above its boiling point, creeps up the sides of the tube, and decomposes at the red-hot parts, yielding ammoniacal gas and a yellow residue of mellone (Liebig):

$$C^6N^6H^6 = C^6N^4 + 2NH^3.$$

Melamine is not, however, a compound of mellone and ammonia; for it cannot be produced by the union of these two bodies, nor does it give off ammonia when treated with hot potash-solution (Liebig). — 2. By boiling with strong nitric acid till it is completely dissolved, or by heating with strong sulphuric acid (which does not blacken it), it is resolved into ammelide and an ammoniacal salt (Liebig):

$$2C^6N^6H^6 + 6HO = C^{12}N^9H^9O^6 + 3NH^3.$$

By continued boiling with dilute nitric acid, melamine is converted, with formation of a continually increasing quantity of ammonia, first into ammeline (which may be precipitated from the acid liquid by ammonia), then into ammelide, and finally, after 12 or 14 hours, into cyanuric acid (Knapp, *Ann. Pharm.* 21, 256):

$$C^6N^6H^6 + 2HO = \underbrace{C^6N^5H^5O^2}_{\text{Ammeline.}} + NH^3.$$

(For the further decomposition of the ammeline and ammelide, see those compounds).— 3. Melamine fused with hydrate of potash, forms cyanate of potash, and if in excess, likewise mellonide of potassium (Liebig). [Probably thus? $C^6N^6H^6 + 3HO + 3KO = 3C^2NKO^2 + 3NH^3$]. — 4. Melamine fused with potassium yields mellonide of potassium, with evolution of ammonia and emission of light and heat (Liebig):

$$C^6N^6H^6 + K = C^6N^4K + NH^3.$$

Combinations. Melamine dissolves sparingly in cold, readily in boiling *water* (Liebig).

It combines as an alkaloid with all acids. When boiled with sal-ammoniac solution, it expels the ammonia, and precipitates the oxide from solutions of manganese, zinc, iron, and copper salts, in some cases, however, but partially, with formation of double salts. The simple *melamine-salts* have a slight acid reaction, are soluble in water, and for the most

part crystallizable; the double salts of melamine are perfectly neutral (Liebig).

Phosphate of Melamine. — The hot, moderately concentrated solution solidifies on cooling, in a white mass consisting of delicate needles, and readily soluble in water (Liebig).

Sulphate of Melamine. — An aqueous solution of melamine, added to dilute sulphuric acid, immediately forms, even when very dilute, a crystalline precipitate which dissolves in hot water, and separates therefrom in short delicate needles on cooling (Liebig).

Hydrochlorate of Melamine.

				Liebig. (*Ann. Pharm.* 26, 187).
6 C	36·0	22·17		22·05
6 N	84·0	51·72		
7 H	7·0	4·31		4·43
Cl	35·4	21·80		
$C^6N^6H^6,HCl$	162·4	100·00		

Nitrate of Melamine. — A hot-saturated solution of melamine in water, mixed with a sufficient quantity of nitric acid to produce a strong acid reaction, solidifies on cooling into a soft mass, which consists of long flexible needles, is permanent in the air, and when burned with oxide of copper, yields 6 vol. carbonic acid gas to 7 vol. nitrogen (Liebig).

Melamine dissolves in *potash-ley* more readily than in water, and crystallizes out from it unchanged (Liebig).

Nitrate of Silver and Melamine. — The hot aqueous solution of melamine, mixed with nitrate of silver, immediately yields a white crystalline precipitate, which increases on cooling, and is not altered by recrystallization.

	Crystallized.		Liebig.
6 C	36	12·16	12·24
7 N	98	33·11	33·06
6 H	6	2·03	2·02
AgO	116	39·19	38·59
5 O	40	13·51	14·09
$C^6N^6H^6,AgO,NO^5$	296	100·00	100·00

Therefore, nitrate of melamine, $C^6N^6H^6,HO,NO^5$, in which HO is replaced by AgO.

Formiate of Melamine. — Shining laminæ, which give off a small quantity of acid on exposure to the air, more quickly at 100°, and dissolve readily in water (Liebig).

Acetate of Melamine. — Large flexible quadratic laminæ, which give off part of their acid at 100°, and dissolve readily in water (Liebig).

Oxalate of Melamine. — Less soluble in water than the nitrate. (Liebig).

				Liebig.
16 C	96	28·07		28·02
12 N	168	49·12		48·67
14 H	14	4·09		3·94
8 O	64	18·72		19·37
$2C^6N^6H^6,C^4H^2O^8$	342	100·00		100·00

Melamine does not dissolve in alcohol or in ether (Liebig).

Appendix to Melamine.

1. Melam. $C^{12}N^{11}H^9=2C^6N^4,3NH^3$?

LIEBIG (1834). *Ann. Pharm.* 10, 10; also *Pogg.* 34, 579. — *Ann. Pharm.* 53, 330; 58, 248.
KNAPP. *Ann. Pharm.* 21, 242.

Remains when sulphocyanide of ammonium is gently heated, whereas at a higher temperature, mellone or a mixture of mellone and melam is produced (VIII, 77).

Preparation. A dry and finely pulverized mixture of 1 pt. sulphocyanide of potassium and 2 pts. sal-ammoniac, is heated, at first somewhat above 100°, then gradually raised to a higher temperature, but not too high, and the melam in the residue freed from chloride of potassium by continued washing with water. Any sulphur that may yet remain, proceeding from the sulphide of potassium produced by too strong heating of the sulphocyanide, may be removed by levigation. Any hydrochloric acid that may remain may be removed by treating the residue with carbonate of potash, and washing. The excess of sal-ammoniac counteracts, by its volatilization, the effects of too strong a heat, by which the melam might be converted into mellone.

To obtain pure melam from this crude product, it is boiled with moderately strong solution of potash till the greater part is dissolved, and the pure melam separated, by cooling the filtrate, in the form of a heavy, white, granular powder (Liebig).

Properties. The substance precipitated from the potash-solution is a heavy, white, granular powder; crude melam is of a yellowish white colour with a tinge of grey, and readily diffuses itself in water in the form of a yellow mud (Liebig).

			Liebig. *a.*	*b.*
12 C	72	30·64	30·49	29·99
11 N	154	65·53	65·57	
9 H	9	3·83	3·94	4·06
$C^{12}H^{11}N^9$	235	100·00	100·00	

The melam *a* was purified by solution in hot potash and cooling; *b* was crude melam, freed from hydrochloric acid by carbonate of potash. Both *a* and *b* yielded by combustion 12 vol. carbonic acid gas to 11 vol. nitrogen.

Gerhardt (*Compt. rend.* 18, 159; also *J. pr. Chem.* 31, 438) formerly

suggested that melam was a mixture of mellone and melamine. But melamine might be extracted by boiling water; and as melam is completely soluble in boiling hydrochloric acid, it cannot contain mellone, which is insoluble in that acid (Liebig). — In a later communication (*N. Ann. Chim. Phys.* 19, 96), Laurent & Gerhardt pronounced melam to be a mixture of mellone and poliene. But mellone is excluded by the above-mentioned behaviour with hydrochloric acid; and poliene, which is the residue obtained by heating pure sulphocyanide of ammonium (p. 484), is identical with melam, when the latter is freed from adhering hydrochloric acid. But the so-called poliene, when examined by the microscope, appears like a mixture of a heavy sandy powder and slender needles, which may be dissolved out by boiling water; whereas melam appears uniform, because in its formation, the effect of too high a temperature has been prevented by the excess of sal-ammoniac present. If, however, melam and poliene be purified by solution in hot potash-ley (p. 482), they exhibit the same composition and the same chemical relations (Liebig).

Völckel regards melam as a mixture of the decomposition-products of poliene, formed when it is somewhat strongly heated, but before it is completely transformed into mellone. [This requires to be proved by actually separating Liebig's melam into these products, and by a more exact description of the products themselves].

Decompositions. 1. Melam is resolved by heat into ammonia, together with a small crystalline sublimate, and a residue of mellone (Liebig). — 2. Its solution in boiling concentrated nitric acid, which is formed without any evolution of nitric oxide, deposits anhydrous cyanuric acid as it cools, while nitrate of ammonia remains in solution (Liebig):

$$C^{12}N^{11}H^9 + 12HO = 2C^6N^3H^3O^6 + 5NH^3.$$

No other acid converts melam into cyanuric acid. — 3. Oil of vitriol decomposes it into ammonia and ammelide (Liebig):

$$C^{12}N^{11}H^9 + 6HO = C^{12}N^9H^9O^6 + 2NH^3.$$

4. Melam boiled with hydrochloric or dilute sulphuric acid dissolves completely, forming a compound of ammonia and ammeline with the acid (Liebig):

$$C^{12}N^{11}H^9 + 4HO = 2C^6N^5H^5O^2 + NH^3.$$

If therefore a solution of melam in dilute sulphuric acid be evaporated beyond the point at which the sulphate of ammeline crystallizes, the ammeline is converted by further ebullition into ammelide (Liebig). The ammelide once formed by the action of comparatively strong sulphuric acid, may then, after the acid has been diluted with water, be decomposed by boiling, into cyanuric acid and ammonia (Knapp). — Concentrated nitric acid likewise converts melam, if the action of heat does not intervene, into ammonia, ammeline, and ammelide (Knapp). If nitric acid of sp. gr. 1·49 be saturated, first in the cold, and afterwards at a gentle heat, with melam, the thickish yellowish solution solidifies on cooling into a pasty mass, from which cold water extracts nitrate of ammonia and ammeline (amounting to 5 per cent of the melam) leaving ammelide, together with a small quantity of ammeline, undissolved (Knapp). — 5. Melam fused with hydrate of potash gives off, with violent frothing, a large quantity of ammoniacal gas; and, if the quantity

of melam be not deficient, leaves a residue of cyanate of potash in a state of tranquil fusion (Liebig):

$$C^{12}N^{11}H^9 + 6(HO,KO) = 6C^2NKO^2 + 5NH^3.$$

6. Melam heated with moderately concentrated potash-ley assumes a yellowish white colour, and breaks up, diffusing itself through the potash in the form of a milky liquid, and after about three days' exposure to the heat of the water-bath dissolves completely, forming a transparent solution. This when evaporated, and still more when cooled, deposits a quantity of melamine amounting to nearly half that of the melam. The mother-liquor contains ammeline (precipitable by acids), together with traces of melamine. There is also produced a small quantity of ammelide, which by longer boiling is resolved into ammonia and cyanuric acid; this explains the evolution of ammonia, which takes place when melam is boiled with potash-ley (Liebig). If the crude melam used in the process contains mellone, arising from the application of too strong a heat in its preparation, the potash-salt described on page 382, is formed at the same time (Liebig). Equation for the formation of melamine and ammeline:

$$C^{12}N^{11}H^9 + 2HO = C^6N^6H^6 + C^6N^5H^5O^2.$$

Combinations. — *Hydrochlorate of Melam.* — After the residue obtained by heating sulphocyanide of potassium with sal-ammoniac (p. 482) has been washed with water, melam remains behind in combination with a small quantity of hydrochloric acid, in the form of a yellow-greyish white powder, which diffuses itself in water like a fine mud. It may be deprived of its hydrochloric acid, not by water, but by aqueous carbonate of potash, and when treated with oil of vitriol, gives off hydrochloric acid gas with strong intumescence (Liebig).

2. Poliene.

VÖLCKEL. *Pogg.* 61, 367; 63, 90.

This, according to Völckel, is a compound isomeric with melamine; according to Liebig, on the contrary, it is identical with melam, a view which is corroborated by the almost identical mode of preparation.

Preparation. Sulphocyanide of ammonium contained in a retort is gradually heated in the oil-bath to 300°; the residue exhausted, first with cold water, then with a small quantity of boiling water, and afterwards repeatedly boiled with water. The first decoction deposits on cooling, another bulky compound; but the following decoctions yield on cooling a white powder of poliene. The substance which remains undissolved after boiling, when freed from two other bodies by treating it with dilute hydrochloric acid and afterwards with boiling dilute potash, also yields poliene, but coloured slightly yellow by a trace of another substance; the residue must therefore be dissolved in boiling water, which, when cooled and evaporated, deposits the poliene in the form of a white powder.

White, or often yellowish white powder (Völckel).

Calc. according to Völckel.			Calc. according to Liebig.			Völckel.
6 C	36	28·57	12 C	72	30·64	28·37
6 N	84	66·67	11 N	154	65·53	
6 H	6	4·76	9 H	9	3·83	4·77
$C^6N^6H^6$	126	100·00	$C^{12}N^{11}H^9$	235	100·00	

Therefore isomeric with melamine (Völckel). As a verification of his analysis, Völckel should have determined the proportions by volume of the carbonic acid and nitrogen gas obtained by combustion (Liebig).

Decompositions. 1. Poliene when heated, swells up, gives off ammonia, and is converted, first into certain intermediate products, among which must be reckoned ammelene = $C^6N^5H^3$, and then into glaucene [mellone] = C^4N^3H. — 2. By boiling with strong hydrochloric acid, it is resolved into ammonia and ammelene, and by cold nitric acid of sp. gr. 1·5, or by oil of vitriol, into ammonia and ammelide, and finally into ammonia and cyanuric acid. [For the equations see melamine, which behaves in the same manner]. — 3. Poliene dissolves readily in strong boiling potash, with evolution of ammonia; if the liquid be filtered before the poliene is entirely dissolved, the filtrate yields on cooling, a heavy white granular powder which, besides nitrogen, contains 30·00 p.c. C and 4·05 H, and is therefore identical in composition with Liebig's pure melam. But it is a mixture of undecomposed poliene ($C^6N^6H^6$) and ammelene ($C^6N^5H^3$), — which are extracted by repeated boiling with water, and deposited as the liquid cools, — and of undecomposed albene, which, besides N and O, contains 29·48 p.c. C and 3·84 H, and yields by combustion 6 vol. carbonic acid gas to 5 vol. nitrogen, and is therefore = $C^{12}N^{10}H^9O^3$. It was formed by access of 3HO to $2C^6N^6H^6$ (poliene) with evolution of $2NH^3$. Albene, by continued boiling with dilute potash, is ultimately converted into ammeline. Hence poliene appears to be converted, first into ammelene, then into albene, and lastly into ammeline. — 5. Poliene boiled with dilute potash dissolves slowly, with evolution of ammonia. The brownish solution, when highly concentrated, yields crystals consisting of cyanurate of potash, of the potash-salt described by Liebig, and of another body, perhaps melamine; the mother-liquor forms with acids a dense white precipitate of melamine. By continued boiling with dilute potash, poliene is completely converted into ammonia and cyanuric acid. — 6. Hydrate of potash, in a state of fusion, decomposes poliene (like melam) into ammonia and cyanic acid:

$$C^6N^6H^6 + 6HO = 3NH^3 + 3C^2NHO^2.$$

Combinations. Poliene dissolves very sparingly in hot *Water*.

With *Acids*, it behaves like a weak base; but even water takes away all the acid, excepting a small quantity which may be extracted by alkalis.

100 pts. of perfectly dry poliene, saturated in a stream of perfectly dry hydrochloric acid gas, and then freed from the excess by a current of dry air, take up about 28·51 pts. of the gas; 100 : 28·51 = 126 : 35·92; therefore $C^6N^6H^6$,HCl.

Poliene is insoluble in alcohol and ether (Völckel).

Unknown Primary Nucleus. C^6H^{12}.

Unknown Oxygen-nucleus. $C^6H^8O^4$.

Glycerine. $C^6H^8O^6 = C^6H^8O^4,O^2$.

SCHEELE. *Opusc.* 2, 175; also *Crell. chem. J.* 4, 190; *Crell. Ann.* 1784, 1, 99 and 2, 328.
FREMY. *Ann. Chim.* 63, 25.
CHEVREUL. *Recherches sur les corps gras.* 209 and 338.
PELOUZE. *Ann. Chim. Phys.* 63, 19; also *Ann. Pharm.* 19, 210 and 20, 46; also *J. pr. Chem.* 10, 287. — Further: *Compt. rend.* 21, 718; also *J. pr. Chem.* 36, 257.
REDTENBACHER. *Ann. Pharm.* 47, 113; 57, 174.
BERTHELOT. On the compounds of Glycerine with Acids. *N. Ann. Chim. Phys.* 41, 216; abstr. *Compt. rend.* 37, 398; 38, 668; *N. J. Pharm.* 24, 259; *Instit.* 1853, 301; *Arch. ph. nat.* 24, 176; *J. pr. Chem.* 60, 193; *Ann. Pharm.* 88, 304; *Pharm. Centr.* 1853, 721, 737; *Chem. Gaz.* 1853, 421; *Chem. Soc. Qu. J.* 6, 280; 7, 282.

Glycerin, Süsses Princip von Scheele, Scheelsches Süss, Ölsüss, Oelzucker, Glyceryloxyd, Principe doux des huiles. — Discovered by Scheele in 1779 in the preparation of lead-plaster.

Occurs in all glycerides (VII, 327) in the form of conjugated compounds with various acids, from which it is separated chiefly by saponification.

Preparation. 1. Five parts of finely triturated litharge are heated with 9 parts of olive-oil or any other glyceride and a small quantity of water, the mixture being constantly stirred and the water renewed, till the lead-oxide is converted into a plaster; the watery liquid separated from this plaster and freed from lead by a small quantity of sulphuric acid or sulphuretted hydrogen; and the filtrate evaporated to a syrup, which is best done over the water-bath (Scheele, Fremy, Chevreul). — 2. A glyceride is saponified with caustic potash; the whole saturated with tartaric acid; the watery liquid separated from the more fixed soapy acids, and evaporated to dryness; the residue exhausted with alcohol of sp. gr. 0·8; the liquid filtered from the tartrate of potash, and again evaporated to dryness; the residue exhausted with absolute alcohol; and the solution again evaporated. — If free tartaric acid is still present, it must be rendered insoluble in alcohol by sufficient addition of potash (Chevreul, *compare* VII, 233). It is difficult by this process to obtain glycerine perfectly free from tartaric acid (Chevreul). — ¶. Riegel (*Jahrb. pr. Pharm.* 21; pt. 3; *Arch. Pharm.* [2], 77, 199) carefully neutralizes the alkaline mother-liquor of the soap-works with sulphuric acid; removes the excess of that acid by digestion with carbonate of baryta; evaporates the filtrate to a syrup; digests it for several days with alcohol; separates the alcoholic liquid from the sulphate of soda which crystallizes out; decolorizes it with animal charcoal, and evaporates to a syrup; again exhausts the residue with strong alcohol; and evaporates the filtered solution in the water-bath. — [On the preparation and purification

of glycerine on the large scale, see also C. Morfit (*Pharm. J. Trans.* 13, 84; *N. J. Pharm.* 24, 357; and Chevallier, *J. Chim. méd.* [3], 9, 465; *Pharm. J. Trans.* 13, 137)]. ¶

To dehydrate completely the glycerine obtained by (1) or (2), it must be left for three months in vacuo over oil of vitriol (Chevreul); or heated in vacuo for several hours to 100°, or in an open vessel over the oil-bath to a temperature between 120° and 130° (Pelouze).

Properties. Colourless or pale yellow, non-crystallizing syrup, which is inodorous, has a sweet taste, and does not redden litmus. Sp. gr. of glycerine dehydrated as completely as possible, 1·27 at 10° (Chevreul); 1·28 at 15° (Pelouze). May be partially distilled by boiling with water (Chevreul).

			Pelouze. *earlier.* sp. gr. 28.		Pelouze. *later.*		Chevreul. sp. gr. 2·7.		Chevreul. sp. gr. 2·52.	
6 C	36	39·13	39·38		39·03		40·07		37·67	
8 H	8	8·70	8·76		8·76		8·92		9·05	
6 O	48	52·17	51·86		52·21		51·01		53·28	
$C^6H^8O^6$	92	100·00	100.00		100·00		100·00		100·00	

Laurent (*Revue scient.* 14, 341) assumes a primary nucleus called *Glycene* = C^6H^{10}, whence he derives the oxygen-nucleus, *Glycose* = $C^6H^6O^4$, and regards glycerine as the alcohol of that nucleus = $C^6H^6O^4,2HO$. — Berzelius (*Jahresber.* 23, 403) proceeds from a radical called *Lipyl* = C^3H^2, which, with 1 At. O, forms *oxide of lipyl* = C^3H^2O; by the addition of 3HO to 2 At. oxide of lipyl ($2C^3H^2O + 3HO$), *hypothetical anhydrous glycerine* = $C^6H^7O^5$ is produced; and this with 1HO forms *hydrate of glycerine*, that is to say glycerine as we know it in the uncombined state. — Liebig and others assume a radical called *Glyceryl*, C^6H^7, which with 5O forms *oxide of glyceryl* = $C^6H^7O^5$; and this with 1HO forms *hydrated oxide of glyceryl* = $C^6H^7O^5,HO$, or glycerine as known in the free state.

Decompositions. 1. Glycerine, when exposed to a heat near to redness, distils for the most part unaltered, but a small portion of it is resolved into a combustible gas, carbonic acid, acrol (p. 365), empyreumatic oil, acetic acid and charcoal. — It first gives off the water that is mixed with it; then below a red heat, a large quantity of glycerine but slightly altered, in the form of a sweet, somewhat empyreumatic syrup; and lastly, at a red heat, it leaves a residue of light shining charcoal, and gives off brown vapours, which condense to a black oil and an acid liquid having a powerful odour and sharp taste. By repeated distillation it may be completely decomposed, the successive distillates exhibiting a continually sharper and more bitter taste (Scheele). — The products obtained by dry distillation are undecomposed glycerine, carbonic acid gas, combustible gas, acetic acid, empyreumatic oil, and charcoal (Fremy, Pelouze). The glycerine at first passes over for the most part undecomposed, together with a very small quantity of acrol, then swells up and froths over (Redtenbacher).

2. In the open fire glycerine burns with a clear flame (Scheele), like an oil (Fremy). — 3. Glycerine dehydrated as completely as possible, and mixed with eight times its weight of platinum-black, becomes heated; absorbs a large quantity of oxygen on exposure to the air, giving off at the same time a vapour which has a slightly acid odour, and reddens litmus; and is converted into a syrupy acid, which has a bitter and sour taste, is neither volatile nor crystallizable, and with the aid of heat, reduces mercurous nitrate and nitrate of silver [propionic acid]. If the experiment be made in oxygen gas over mercury, copious absorption takes place, attended with evolution of heat, and is completed in a few

hours; and the glycerine is converted, with formation of carbonic acid, into the above acid, which, if the mixture be kept in the atmosphere of oxygen for several days, is completely resolved into carbonic acid and water; in this reaction, 1 At. $C^6H^8O^6$ consumes $13\frac{1}{3}$ At. O (Döbereiner, *J. pr. Chem.* 28, 499; 29, 451). — 4. Glycerine dissolved in a large quantity of water, and exposed to the air for several months at 20° or 30°, in contact with well washed yeast, is converted, with evolution of a few gas-bubbles, into propionic acid (Redtenbacher, p. 402, 4). — 5. Every time that an aqueous solution of glycerine is evaporated, a coloured substance is formed, which gives a precipitate with subacetate of lead. The lead-precipitate, washed and decomposed by sulphuretted hydrogen, yields a colourless filtrate, which, when evaporated, first assumes a yellow, then a brown colour, brown drops of liquid forming at the bottom and rising through the liquid, and leaves a brown transparent residue, which dissolves with turbidity in water, but completely in potash-ley, forming a brown solution. When aqueous glycerine is evaporated in vacuo, a substance is produced which colours the glycerine yellow, and is not precipitated by subacetate of lead (De Jough, *Berzelius, Jahresber.* 23, 405). — 6. In a bottle filled with chlorine gas, glycerine is converted, in the course of several months, with formation of hydrochloric acid gas, into a syrup, from which water separates numerous flakes of a white, fusible substance, which has an unpleasant ethereal odour, and a very sour, bitter and harsh taste (Pelouze). — 7. It dissolves a large quantity of bromine, with evolution of heat; after it has been saturated with bromine while warm, water takes up from the solution a large quantity of hydrobromic acid, and separates a heavy oil, having an unpleasant ethereal odour, soluble in ether and alcohol, and precipitable from the latter by water; its formula is $C^{12}H^{11}Br^3O^{10}$ (Pelouze). — 8. Glycerine is rapidly decomposed by peroxide of manganese and hydrochloric or dilute sulphuric acid, yielding carbonic and a large quantity of formic acid (Pelouze). — 9. It is converted by nitric acid into oxalic acid, but only after repeated evaporation (Scheele); it is very easily decomposed by nitric acid, yielding water, carbonic acid, oxalic acid, and nitrous fumes (Pelouze). — 10. When syrupy glycerine is acted upon at ordinary temperatures by a mixture of 2 vol. oil of vitriol, and 1 vol. strong nitric acid, violent action takes place, and nothing is formed but products of oxidation; but if the mixed acids be cooled by a freezing mixture and the glycerine dropped in, with constant stirring, it dissolves quietly; and on shaking up the solution with water, an oil separates out, which, when washed with water, then dissolved in alcohol and precipitated by water, or dissolved in ether, recovered by evaporation, and then dried in vacuo over oil of vitriol, exhibits a pale yellow colour; is much heavier than water; inodorous; has a sweet, pungent and aromatic taste; but if placed on the tongue even in very small quantity, produces headache, which lasts for several hours. [Doubtless a nitro-compound, p. 501]. (Sobrero, *Compt. rend.* 24, 247). — 11. Glycerine subjected to dry distillation in contact with bisulphate of potash, yields sulphurous acid, acrol, acrylic acid, a number of secondary products, and a viscid carbonaceous residue; it behaves in a similar manner with oil of vitriol, excepting that in this case, no acrol is obtained (Redtenbacher). — 12. Mixed with anhydrous phosphoric acid, it becomes heated, gives off the odour of acrol; and if afterwards distilled, yields acrol and other products, the residue swelling up and charring (Redtenbacher):

$$C^6H^8O^6 = C^3H^4O^2 + 4HO.$$

¶ 13. When glycerine is slowly added to pentachloride of phosphorus, great heat is evolved, hydrochloric acid is disengaged in abundance, and the mixture becomes viscid, and hardens on cooling. On treating the residue with water, or better with carbonate of soda, a substance separates which is heavier than water, and resembles precipitated silica. If the glycerine be added in the state of dilute solution to the chloride of phosphorus, or if too much of it be added at once, the chief products formed are phosphoric and hydrochloric acid, which decompose and dissolve the above-mentioned product. The latter, after complete washing with water, contains chlorine, but no phosphorus. It dissolves readily in hot nitric acid and in cold potash, slowly in boiling aqueous ammonia or in boiling acetic acid. It is not precipitated from either of these solutions by neutralizing the liquid. It is insoluble in alcohol and in ether. In cold water it remains unaltered; but boiling water dissolves it slowly, forming a solution, which yields by evaporation, a hard transparent substance which absorbs aqueous vapour in considerable quantity (Duffy, *Chem. Soc. Qu. J.* 5, 303). ¶.

14. Glycerine treated with biniodide of phosphorus, yields gaseous propylene, C^6H^6, a distillate of water and iodopropylene, C^6H^5I, and a residue containing certain oxygen-acids of phosphorus, together with free iodine, undecomposed glycerine and a trace of red phosphorus (Berthelot & De Luca, *Compt. rend.* 19, 745):

$$2C^6H^8O^6 + PI^2 + C^6H^5I + 4HO + I + (C^6H^8O^6 + PO^3 - HO).$$

The formation of iodopropylene is due to a reducing action exerted by the PI^2 on the glycerine. The liberation of C^6H^6 appears to be of secondary importance (Berthelot & De Luca; *comp.* p. 395). ¶.

15. Glycerine mixed with hydrate of potash and gently heated, gives off a large quantity of hydrogen gas, and leaves a white mass consisting of acetate and formiate of potash (Dumas & Stas, *Ann. Chim. Phys.* 73, 148; also *Ann. Pharm.* 35, 158):

$$C^6H^8O^6 + 2KO = C^4H^3KO^4 + C^2HKO^4 + 4H.$$

The first products are acrylate of potash and acrol, inasmuch as the glycerine, by giving up 4HO to the potash, which thereby becomes more fluid, is converted into acrol, which, if the heat be afterwards increased till the mass becomes white, gives off hydrogen, and is converted into acrylate of potash; and this compound is, by the further action of the potash-hydrate, for the most part resolved into acetate and formiate of potash (Redtenbacher):

First:

$$C^6H^8O^6 - 4HO = C^6H^4O^2;$$

then:

$$C^6H^4O^2 + KO,HO = C^6H^3KO^4 + 2H;$$

finally:

$$C^6H^3KO^4 + KO + 3HO = C^4H^3KO^4 + C^2HKO^4 + 2H.$$

16. Glycerine boiled with cupric acetate or sulphate, throws down a very small quantity of cuprous oxide (A. Vogel, *Schw.* 13, 167). — ¶ John (*Arch. Pharm.* [2] 68, 37, *Pharm. Centr.* 1851, 927), by boiling glycerine with cupric sulphate, obtained a precipitate of cupric hydrate, but no metallic copper. ¶ — Glycerine boiled with aqueous terchloride of gold, throws down a dark purple powder (Vogel).

Glycerine dissolved in 4 pts. of water remains unaltered for months (Scheele); it is not brought into the state of vinous fermentation by yeast (Fremy, Pelouze).

Combinations. Glycerine deliquesces in the air, and mixes in all proportions with *Water*. The aqueous solution evaporated in the air at 100°, leaves a syrup of sp. gr. 1·252 at 17°, still containing 6 p.c. water (Chevreul).

It dissolves a large quantity of *Iodine*, with orange-yellow colour and without decomposition (Pelouze).

It forms with *Potash* a compound soluble in alcohol, and therefore mixes without precipitation with alcoholic potash (Scheele). — With *Baryta*, *Strontia* and *Lime*, it forms compounds soluble in water, sparingly soluble in alcohol, and not precipitated by carbonic acid (Chevreul). — Glycerine, even when dehydrated as completely as possible, dissolves potash, soda, baryta and strontia, the first two abundantly (Pelouze).

Anhydrous glycerine dissolves all deliquescent salts and many others, *e. g.* the sulphates of potash, soda, and copper, the nitrates of soda and silver, the chlorides of potassium and sodium (Pelouze).

Aqueous glycerine (Fremy), and even the anhydrous compound (Pelouze) dissolves *protoxide of lead*, and consequently does not precipitate subacetate of lead (Fremy).

Other bodies insoluble in water are not dissolved by anhydrous glycerine (Pelouze).

Sesquichloride of iron mixed with a large quantity of glycerine is not precipitated by alkalis or alkaline hydrosulphates (H. Rose).

Cupric sulphate or acetate mixed with glycerine forms a clear azure-blue mixture with excess of potash (A. Vogel). — Cupric sulphate mixed with glycerine forms with a small quantity of potash a precipitate which dissolves in a larger quantity; but the resulting blue solution decomposes even below 100°, depositing bluish flakes (Lassaigne, *J. Chim. med.* 18, 447).

Glycerine dissolves in alcohol in all proportions, but not in ether (Lecanu, Pelouze). — It dissolves many *Vegetable Acids* (Pelouze).

¶ The compounds of glycerine with acids have lately been made the subject of an elaborate investigation by Berthelot, from which it appears that glycerine is capable of uniting *directly*, both with the fatty acids (stearic, margaric, &c.) properly so called, and with other acids both organic and inorganic. — The union is effected by prolonged contact of the acid and glycerine in sealed tubes at a temperature more or less elevated. Nearly all the compounds form likewise at ordinary temperatures, but very slowly. In certain cases, they are obtained by double decomposition between glycerine and compound ethers. They may also be formed by the action of hydrochloric acid on a mixture of glycerine and the acid.

The bodies thus formed are neutral, and incapable of uniting with alkalis; some of them are crystalline, others liquid. They all, when treated with alkalis, slowly reproduce the original acid and glycerine. Strong hydrochloric acid decomposes them in a similar manner. When treated with alcohol and hydrochloric acid, they yield glycerine and an ether of the acid previously united therewith: these two reactions they exhibit in common with the natural fats. All of them, excepting two, which are volatile, are decomposed by heat, and yield acrol. Lastly, ammonia converts them into amides.

From these facts it appears that the glycerine-salts are analogous to compound ethers of the third class (VII, 215), and consequently that glycerine is analogous to alcohol:

A compound ether = Acid + Alcohol − Water
A glycerine-salt = Acid + Glycerine − Water.

Moreover, by the action of alkalis, of concentrated acids, and of water, either quickly at high, or slowly at ordinary temperatures, the neutral fats or glycerine-salts are resolved into acids and glycerine, and the ethers in like manner, into acids and alcohol.

The compounds of glycerine with acids may be arranged in three series. Those of the first series, which are analogous to the compound ethers, are formed by the union of 1 At. of an acid and 1 At. glycerine, with separation of 2 At. water; *e.g.*

Monoacetin	$C^{10}H^{10}O^8$	=	$C^4H^4O^4$	+	$C^6H^8O^6$	−	2HO
Monobutyrin	$C^{14}H^{14}O^8$	=	$C^8H^8O^4$	+	$C^6H^8O^6$	−	2HO
Monovalerin	$C^{16}H^{16}O^8$	=	$C^{10}H^{10}O^4$	+	$C^6H^8O^6$	−	2HO
Monostearin	$C^{42}H^{42}O^8$	=	$C^{36}H^{36}O^4$	+	$C^6H^8O^6$	−	2HO
Monochlorhydrin	$C^6H^7ClO^4$	=	HCl	+	$C^6H^8O^6$	−	2HO.

The second series is formed by the union of 2 At. acid and 1 At. glycerine, with separation of 2 [?] or 4 At. water: *e.g.*

Biacetin	$C^{14}H^{12}O^{10}$	=	$2C^4H^4O^8$	+	$C^6H^8O^6$	−	4HO
Bibutyrin	$C^{22}H^{22}O^{12}$	=	$2C^8H^8O^4$	+	$C^6H^8O^6$	−	2HO [?]
Bivalerin	$C^{26}H^{26}O^{12}$	=	$2C^{10}H^{10}O^4$	+	$C^6H^8O^6$	−	2HO [?]
Bistearin	$C^{78}H^{78}O^{12}$	=	$2C^{36}H^{36}O^4$	+	$C^6H^8O^6$	−	2HO [?]
Biethylin	$C^{14}H^{16}O^6$	=	$2C^4H^6O^2$	+	$C^6H^8O^6$	−	4HO
Bichlorhydrin	$C^6H^6Cl^2O^2$	=	2HCl	+	$C^6H^8O^6$	−	4HO
Benzochlorhydrin	$C^{20}H^{11}ClO^6$	=	$C^{14}H^6O^4 + HCl$	+	$C^6H^8O^6$	−	4HO

The third series results from the union of 3 At. acid and 1 At. glycerin, with separation of 6 At. water: *e. g.*

Triacetin	$C^{18}H^{14}O^{12}$	=	$3C^4H^4O^4$	+	$C^6H^8O^6$	−	6HO
Tributyrin	$C^{30}H^{26}O^{12}$	=	$3C^8H^8O^4$	+	$C^6H^8O^6$	−	6HO
Trivalerin	$C^{36}H^{32}O^{12}$	=	$3C^{10}H^{10}O^4$	+	$C^6H^8O^6$	−	6HO
Tristearin	$C^{114}H^{110}O^{12}$	=	$3C^{36}H^{36}O^4$	+	$C^6H^8O^6$	−	6HO
Triolein	$C^{114}H^{104}O^{12}$	=	$3C^{36}H^{34}O^4$	+	$C^6H^8O^6$	−	6HO.

The bodies of this last series are perfectly identical, in properties and composition with the natural fats, stearin, olein, &c. (Berthelot).

[The bodies of the first series may be regarded as glycerine in which 1 At. H is replaced by the radical of the acid, or again as glycerine coupled with 1 At. of an oxygen-nucleus derived from the primary nucleus of the series to which the acid belongs, by the substitution of 2O for 2H; thus, monoacetin may be regarded as glycerine in which 1 At. H is replaced by 1 At. othyl, $C^4H^3O^2$, or as 1 At. glycerine coupled with 1 At. of the oxygen-nucleus $C^4H^2O^2$ (othylene) formed from ethylene, C^4H^4, by the substitution of 2O for 2H:

$$C^{10}H^{10}O^8 = C^6\left\{\begin{matrix}H^7\\C^4H^3O^2\end{matrix}\right\}O^6 = C^6H^8O^6, C^4H^2O^2;$$

similarly, for monovalerin:

$$C^{16}H^{16}O^8 = C^6\left\{\begin{matrix}H^7\\C^{10}H^9O^2\end{matrix}\right\}O^6 = C^6H^8O^6, C^{10}H^8O^2.$$

The bodies of the second series (with some apparent exc
be regarded as glycerine in which 2 At. H are re

radical, or as 1 At. glycerine coupled with 2 At. of the corresponding nucleus; thus for biacetin, we have:

$$C^{14}H^{12}O^{10} = C^6\left\{\begin{matrix}H^6\\(C^4H^3O^2)\end{matrix}\right\}O^6 = C^6H^8O^6,(C^4H^2O^2)^2;$$

and for biethylin:

$$C^{14}H^{16}O^6 = C^6\left\{\begin{matrix}H^6\\(C^4H^5)^2\end{matrix}\right\}O^6 = C^6H^8O^6,(C^4H^4)^2.$$

But bibutyrin, bivalerin, and bistearin appear to deviate from this law, inasmuch as (according to Berthelot's analyses), their formation is attended with the elimination of only 2 At. water instead of 4 At. As however the purification of these substances is attended with considerable difficulty, it is probable that the anomaly is only apparent and will be removed by further investigation According to the above law, the formula of bibutyrin should be:

$$C^{22}H^{20}O^{10} = C^6\left\{\begin{matrix}H^6\\(C^8H^7O^2)^2\end{matrix}\right\} = C^6H^8O^6,(C^8H^6O^2)^2;$$

and similarly for the rest.

The bodies of the third series may be regarded as glycerine in which 3 At. H are replaced by a radical, or as 6 At. glycerine coupled with 3 At. of the corresponding nucleus: *e.g.* for triacetin, and tristearin:

$$C^{18}H^{14}O^{12} = C^6\left\{\begin{matrix}H^3\\(C^4H^3O^2)^3\end{matrix}\right\}O^6 = C^6H^8O^6,(C^4H^2O^2)^3$$

$$C^{114}H^{110}O^{12} = C^6\left\{\begin{matrix}H^3\\(C^{36}H^{35}O^2)^3\end{matrix}\right\}O^6 = C^6H^8O^6,(C^{36}H^{34}O^2)^3.$$

The chlorhydrins belong altogether to a different type; see page 498. [W]. ¶

Conjugated Compounds of Glycerine.

Phosphoglyceric Acid. $C^6H^8O^6,HO,PO^5$.

PELOUZE (1845). *Compt. rend.* 21, 718; also *J. pr. Chem.* 36, 257.
GOBLEY. *N. J. Pharm.* 9, 161; 11, 409; 12, 5.

Glycerin-phosphorsäure, Acide phosphoglycerique. Occurs [in the form of a peculiar compound with oleic and margaric acid] in the yolk of eggs and in the brain (Gobley).

Preparation. Glycerine mixes with an excess of anhydrous phosphoric acid or its solid hydrate, the temperature of the mixture rising above 100°, and a large quantity of phosphoglyceric acid being formed. The mixture is dissolved in water; neutralized, first with carbonate of baryta, and then with baryta-water; filtered from the phosphate of baryta; and the baryta precipitated from the filtrate by an equivalent quantity of sulphuric acid: the filtered liquid is an aqueous solution of phosphoglyceric acid (Pelouze).

To obtain this acid from yolk of egg, that substance is freed from the greater part of its water by heat; then exhausted with boiling alcohol or ether; the filtrate evaporated; the residue consisting of egg-oil and a viscid substance (*matière visqueuse*), collected on a filter, and left to drain

in the hot air chamber till the greater part of the oil has run off; and the residual viscid matter pressed between folds of paper, renewed as often as any oil is thereby extracted. The soft, orange-yellow, translucent mass, smelling of yolk of egg, is then heated with dilute potash in the water-bath for 24 hours; the solution slightly supersaturated with acetic acid; filtered from oleic, margaric acid, &c.; the filtrate precipitated with neutral acetate of lead; the precipitated phosphoglycerate of lead washed, suspended in water, and decomposed by sulphuretted hydrogen; the filtrate concentrated by gentle evaporation, and freed from a small quantity of hydrochloric acid by agitation with a small quantity of oxide of silver, and filtration; the silver precipitated by sulphuretted hydrogen; the filtered liquid freed from a small quantity of acid phosphate of lime by saturation with lime-water; the liquid separated by filtration from the phosphate of lime; and the solution of phosphoglycerate of lime evaporated to the crystallizing point. The crystals are purified by again dissolving them in water, filtering, and evaporating to the crystallizing point; the lime precipitated from their aqueous solution by an equivalent quantity of oxalic acid; and the filtrate evaporated in vacuo (Gobley).

Properties. Viscid mass, having a very sour taste (Gobley). According to Pelouze, the aqueous acid cannot be concentrated beyond a certain point without decomposing, even in the cold: hence the mass obtained by Gobley doubtless contained free phosphoric acid and glycerine.

Decompositions. The acid when ignited leaves a very acid charcoal. Its solution in 10 pts. or more of water may be boiled without decomposition; but a more concentrated solution is decomposed thereby, with liberation of phosphoric acid (Gobley).

Combinations. The acid dissolves readily in *Water* (Gobley).

Its salts are generally soluble in water, but insoluble or very sparingly soluble in alcohol (Pelouze).

Phosphoglycerate of Baryta. — Soluble in water, and precipitated from the solution by alcohol (Pelouze).

	Dried at 150°.			Pelouze.
$3\,BaO,PO^5$	224·6	....	73·02	 73
$C^6H^7O^5$	83·0	....	26·98	
$C^6H^6Ba^2O^6,HO,PO^5$	307·6	....	100·00	

Pelouze states that 1·916 pts. of the salt leave, when ignited, 1·246 pts. of phosphate of baryta, therefore 73 per cent; but 1·916 : 1·1246 = 100 : 65·05; one of his numbers is therefore incorrect.

Phosphoglycerate of Lime. — Snow-white, pearly laminæ, inodorous, but having a rather sharp taste (Gobley). Sustains a heat of 170° without decomposition (Pelouze); blackens at a somewhat stronger heat (Gobley). When boiled down with lime and water, it is resolved into phosphate of lime and glycerine, which may be dissolved out by alcohol (Gobley). Dissolves much more abundantly in cold than in boiling water, so that it separates almost completely from the cold solution on boiling; from the aqueous solution it is precipitated by alcohol (Pelouze, Gobley).

			Pelouze. *dried at* 165°.	Gobley. *dried at* 120°.
2 CaO,PO^5	127·4	60·55	60·10	60·27
6 C	36·0	17·11	17·00	17·05
7 H	7·0	3·33	3·42	3·49
5 O	40·0	19·01	19·48	19·19
$C^6H^6Ca^2O^6,HO,PO^5$	210·4	100·00	100·00	100·00

Phosphoglycerate of Lead. — Insoluble in water. After drying at 120°, it leaves on ignition 77·5 p.c. diphosphate of lead, and is therefore $C^6H^6Pb^2O^6,HO,PO^5$ (Pelouze).

Sulphoglyceric Acid. $C^6H^8O^6,2SO^3$.

Pelouze (1836). *Ann. Chim. Phys.* 63, 21; also *Ann. Pharm.* 19, 211; 20, 212; also *J. pr. Chem.* 10, 289.

Glycerin-Schwefelsäure, Acide sulfoglycerique.

Preparation. — 1 pt. of glycerine is mixed with 2 pts. oil of vitriol, whereupon a considerable evolution of heat takes place; the mass, when cold, dissolved in water; the solution saturated with lime, filtered, and evaporated to a syrup; the crystals of the lime-salt which separate on cooling, collected and dissolved in water; the lime precipitated from the solution by the proper quantity of oxalic acid; and the liquid filtered.

By this process, *aqueous sulphoglyceric acid* is obtained in the form of a colourless, inodorous, strongly acid liquid, which may be evaporated in vacuo, even at a temperature a few degrees below 0°, and when moderately concentrated, does not resolve itself into free sulphuric acid and glycerine.

The aqueous acid decomposes carbonates. The *sulphoglycerates* decompose with great facility and are very soluble in water. (The potash-salt and the lime-salt yield by dry distillation, sulphurous acid, acrylic acid, acrol, and secondary products of decomposition. Redtenbacher, *Ann. Pharm.* 47, 118).

Sulphoglycerate of Baryta. — Its aqueous solution heated with baryta is resolved, even below 100°, into sulphate of baryta which is precipitated, and an aqueous solution of glycerin.

Sulphoglycerate of Lime. — The aqueous acid neutralized at a moderate heat with milk of lime, then filtered and evaporated to a syrup, yields on cooling, colourless needles which have a bitter taste. The salt begins to decompose between 140° and 150°, emitting an intolerable odour of distilled tallow (of acrol, according to Redtenbacher), and leaves, first a carbonaceous residue, then a white residue of sulphate of lime. This residue moistened with sulphuric acid and again ignited, amounts to 35·4 p.c. of the salt dried at 120°. — The aqueous solution of the salt is not decomposed by lime-water at ordinary temperatures, and therefore does not subsequently precipitate chloride of barium; but after boiling for a short time with lime-water, it contains sulphate of lime, and consequently forms a precipitate with chloride of barium. The crystallized salt dissolves in less than 1 pt. of water, but not in alcohol or ether.

	Dried at 100°.		Pelouze.
CaO	28	14·66	14·58
2 SO^3	80	41·88	41·22
6 C	36	18·85	18·85
7 H	7	3·66	3·70
5 O	40	20·95	21·65
$C^9H^7CaO,2SO^3$	191	100·00	100·00

The *Lead-salt* has a similar constitution, and is soluble in water; so likewise is the silver-salt (Pelouze).

Dulk (*Berl. Jahrb.* 1821, 166), by treating olive-oil with oil of vitriol, obtained a *sulpholeous acid* (*schwefelölige Säure*) forming with baryta a soluble, crystallizable, bitter salt which charred in the fire, with tumefaction and slight inflammation; the presence of sulphur in this acid was not however demonstrated.

It may be assumed, with much greater confidence, that the acid described in 1823 by Chevreul (*Recherches sur les corps gras*, 457) under the name of *Sulpho-adipic acid*, is identical with the sulphoglyceric acid of Pelouze. Chevreul heated a mixture of equal parts of hog's lard and oil of vitriol to 100° for a few minutes; mixed it with water, slightly supersaturated the filtrate with baryta-water; filtered again, and evaporated the filtrate to dryness; washed the residue with water; dissolved it in alcohol; and by evaporating the filtrate, obtained an uncrystallizable baryta-salt, which had a pungent and afterwards sweetish taste, and when heated gave off, besides sulphur, sulphurous acid, and sulphuretted hydrogen, a vapour having a sour, empyreumatic and very pungent odour, and left a residue of sulphide of barium mixed with charcoal. By decomposing the aqueous solution of the baryta-salt with sulphuric acid, and filtering, Chevreul obtained the aqueous acid, which when evaporated, formed a very sour syrup, yielding when heated, products similar to those obtained from the baryta-salt, and emitting a still more pungent odour.

¶ Biethylin. $C^{14}H^{16}O^6=(C^4H^4)^2,C^6H^8O^6=C^6\left\{\begin{matrix}H^6\\(C^4H^5)^2\end{matrix}\right\}O^6$.

Berthelot. *N. Ann. Chim. Phys.* 41, 305.

Diethyline (Berthelot); *Biethyloglycerine.*

Formation and Preparation. By the action of hydrobromic ether on glycerine in presence of potash.

$$C^6H^8O^6 + 2C^4H^5Br = 2HBr + C^{14}H^{16}O^6.$$

A mixture of glycerine, hydrobromic ether, and excess of potash is heated in a sealed tube to 100° for 24 hours. Two liquids are then found in the tube, the lower consisting of glycerine and bromide of potassium partly crystallized; the upper of undecomposed hydrobromic ether and biethylin. On distilling this upper layer, the hydrobromic ether distils over at 40°, and almost immediately afterwards, the temperature rises to 191°, at which point the biethylin distils over.

Properties. Transparent, colourless oil, tolerably mobile. Sp. gr. 0·92 Boils at 191°. Odour ethereal and somewhat peppery (Berthelot).

			Berthelot (*mean*).
14 C	84	56·7	56·0
16 H	16	10·8	10·8
6 O	48	32·5	33·2
$C^{14}H^{16}O^8$	148	100·0	100·0

May be regarded as a conjugate compound of 2 At. ethylene with 1 At. glycerine, or as glycerine in which 2 At. H are replaced by ethyl. [W].

Biethyline enclosed in a sealed tube with pure lime, and heated at one end with the precaution of returning the liquid to the red-hot lime, emits an odour of acrol. — Distilled with a mixture of 1 pt. sulphuric and 8 pts. of butyric acid, it yields butyric ether (Berthelot).

¶ Acetin. $C^{10}H^{10}O^8 = C^4H^2O^2, C^6H^8O^6 = C^6\left\{\begin{matrix}H^7\\(C^4H^3O^2)\end{matrix}\right\}O^6$.

Berthelot. *N. Ann. Chim. Phys.* 41, 277.

Monoacétine, Othyloglylcerine.

Obtained by heating a mixture of glycerine and glacial acetic acid to 100° for 24 hours. — An acetin is also formed, but in very minute quantity, when the two liquids are left in contact for three months at ordinary temperatures. — Hydrochloric acid heated to 100° with acetic acid and glycerine, yields after 9 days, an acetin mixed with chlorhydrin. — Acetin is not obtained by distilling glycerine with a mixture of sulphuric and acetic acid (Berthelot).

Neutral liquid having a slightly ethereal odour. Sp. gr. 1·20.

			Berthelot (*mean*).
10 C	60	44·8	45·8
10 H	10	7·5	7·5
8 O	8	47·7	46·7
$C^{10}H^{10}O^8$	78	100·0	100·0

May be regarded as 1 At. glycerine coupled with 1 At. othylene (a nucleus derived from ethylene, C^4H^4, by the substitution of 2O for 2H), or as glycerine in which 1 At. H is replaced by othyl. [W.]

Acetin treated with alcohol and hydrochloric acid, yields glycerine and acetic ether. — Mixed with half its bulk of water, it forms a clear liquid, which becomes turbid on the addition of two more volumes of water, but the acetin does not separate from it; the emulsion continues opalescent, notwithstanding the addition of a large quantity of water.

Acetin mixes with *ether* (Berthelot).

¶ Biacetin. $C^{14}H^{12}O^{10} = (C^4H^2O^2)^2, C^6H^8O^6 = C^6\left\{\begin{matrix}H^6\\(C^4H^3O^2)^2\end{matrix}\right\}O^6$.

Berthelot. *N. Ann. Chim. Phys.* 41, 278.

Diacétine, Biothyloglycerine, Acetidine.

Obtained: 1. By heating glacial acetic acid with excess of glycerine to 200° for three hours. — 2. By heating the same two liquids together

to 275°. — 3. By heating glycerine to 200° with acetic acid diluted with an equal bulk of water. — 4. By heating to 200° a mixture of 1 pt. glycerine and 4 or 5 pts. acetic acid. — The product is purified by saturating the free acid with carbonate of potash and distilling. — The liquid thus neutralized often separates into two layers, each of which contains an acetin; the upper liquid appears also to contain an *acetoglycerate of potash*.

Biacetin is a neutral odoriferous liquid, having a sharp taste. When carefully heated, it boils at 280°, and distils without alteration. Sp. gr. of the distilled product = 1·184 at 16·5°; of another sample, prepared at 170° and not distilled, 1·188 at 13°. When cooled to −40°, it assumes a viscid consistence, like olive oil on the point of solidifying.

			Berthelot (*mean*).
14 C	84	47·8	47·5
12 H	12	6·8	7·1
10 O	10	45·4	45·4
$C^{14}H^{12}O^{10}$	106	100·0	100·0

Biacetin, like acetic ether, becomes slightly acid by contact with the air; in 2½ months in the dark, it absorbs 1 per cent of oxygen. In contact with brass, it absorbs, like acetic ether, 5 per cent in the same time. — Treated, in the cold, with hydrochloric acid and alcohol, it yields acetic ether and glycerine. — Treated with baryta, it yields syrupy glycerine and acetate of baryta, which may be separated by cold alcohol; 100 pts. of biethylin thus treated yield a quantity of acetate of baryta corresponding to 66·4 pts. of acetic acid, and 52·4 of glycerine, making together 118·8 pts.; calculation requires 68·2 pts. acetic acid and 52·3 glycerine, making together 120·5 pts.

Biacetin mixes with *Ether* and dissolves in *Benzine*, but is nearly or quite insoluble in bisulphide of carbon (Berthelot).

¶ Triacetin. $C^{18}H^{14}O^{12} = (C^4H^3O^2)^3, C^6H^8O^6 = C^6\left\{\begin{matrix}H^5\\(C^4H^3O^2)^3\end{matrix}\right\}O^6$.

Berthelot. *N. Ann. Chim. Phys.* 41, 282.

Triethylin, Triethyloglycerine.

Obtained by heating biacetin to 250° for three hours with 15 to 20 times its weight of glacial acetic acid.

Neutral, odoriferous liquid, having a sharp and somewhat bitter taste. Sp. gr. 1·174 at 8°. Volatilizes without residue.

			Berthelot (*mean*)
18 C	108	49·6	49·9
14 H	14	6·4	6·8
12 O	96	44·0	43·3
$C^{18}H^{14}O^{12}$	218	100·0	100·0

Triacetin treated at ordinary temperatures with alcohol and hydrochloric acid, yields acetic ether and glycerine. — With baryta, it yields glycerine and acetate of baryta. 100 pts. thus treated yielded 80·6 pts. acetic acid and 43·1 glycerine = 123·7; calculation requires 82·6 acetic acid and 42·2 glycerine = 124·8.

Triacetin is insoluble in water, and does not mix with it. Dissolves very readily in dilute *alcohol* (Berthelot).

A compound of acetic acid and glycerine, probably triacetin, appears to exist in cod-liver oil (Jeugh, *Berz. Jahresber.* 1843), and in considerable quantity in the oil of *Euonymus europæus* (Schweizer, *J. pr. Chem.* 53, 437; *Ann. Pharm.* 80, 288; *Jahresber. L. & K.* 1851, 444).

¶. *Chlorine-nucleus.* $C^6H^7ClO^4$.

Chlorhydrin. $C^6H^7ClO^4$.

BERTHELOT. *N. Ann. Chim. Phys.* 41, 296.

Monochlorhydrine.

Obtained by saturating gently heated glycerine with hydrochloric acid gas:

$$C^6H^8O^4 + HCl = C^6H^7ClO^4 + 2HO.$$

The liquid, after saturation, must be kept at a temperature of 100° for 36 hours; otherwise the product is extremely small. The solution is then saturated with carbonate of soda, agitated with ether, and the ether evaporated. On distilling the residue, the chlorhydrin distils over at 227°. It must be treated once more with carbonate of soda and ether. — A chlorhydrin is also obtained, but in very small quantity, by slowly distilling glycerine in a stream of hydrochloric acid gas.

Neutral oil, having a fresh ethereal odour and a sweet taste, with pungent after-taste. Sp. gr. 1·31. Retains its fluidity perfectly at −35°. Boils at 227°.

				Berthelot.
6 C	48·0	32·6		32·9
7 H	7·0	6·3		6·8
Cl	35·4	32·1		30·8
4 O	32·0	29·0		29·5
$C^6H^7ClO^4$	122·4	100·0		100·0

May be regarded as *chloride of glycyl*, $C^6H^7O^4,Cl$, or as a chlorine-nucleus derived from the oxygen-nucleus $C^6H^8O^4$, by the substitution of 1Cl for 1H.

Chlorhydrin burns with a white, green-edged flame, emitting hydrochloric acid. — Oxide of lead saponifies it slowly and with difficulty, yielding quantities of glycerine and hydrochloric acid nearly proportional to the atomic weights of those bodies. — Does not precipitate nitrate of silver, at least not immediately.

Chlorhydrin mixes with its own bulk of *Water*. With 8 or 10 times its bulk of water, it forms a very stable emulsion, which remains unaltered, after being left at rest for a month. — It also mixes with *Ether* (Berthelot).

ACETO-CHLORHYDRIN. $C^{10}H^9ClO^6 = C^6H^7ClO^4 + C^4H^2O^2$. Obtained, together with bichlorhydrin, by passing hydrochloric acid gas to saturation through a mixture of acetic acid and glycerine kept at a temperature of 100° for several hours; leaving the liquid to itself for several days or weeks; and then saturating it with carbonate of soda. Acetochlorhy-

drin then separates in the form of a neutral oil, very fluid, nearly insoluble in water, and having a very decided odour, like that of acetic acid. It remains liquid at −40°, but solidifies in a transparent mass at −78°. Boils between 180° and 200°. By analysis it was found to contain 31·9 p.c. C, 5·2 H, and 40·0 Cl. The above formula requires 39·4 C, 5·9 H, and 23·3 Cl, and that of bichlorhydrin (*inf.*), gives 27·9 C, 4·7 H, and 54·6. The composition of the oil is therefore that of a mixture of acetochlorhydrin and bichlorhydrin. By repeated fractional distillation, a substance separates from it which boils at 180° and appears to be bichlorhydrin; the remainder boils between 190° and 230°, without exhibiting a fixed boiling point.

Acetochlorhydrin may be regarded as chlorhydrin having 1 At. H replaced by othyl, $C^4H^3O^2$; or as 1 At. chlorhydrin coupled with 1 At. othylene, $C^4H^3O^2$ (Berthelot, *N. Ann. Chim. Phys.* 41, 303).

The three following compounds are derived from different nuclei.

Bichlorhydrin, $C^6H^6Cl^2O^2$. — Obtained by dissolving glycerine in 10 or 12 times its weight of fuming hydrochloric acid, and heating the solution to 100° for three or four days; then saturating with carbonate of potash, agitating with ether, and evaporating the ether, first in the water-bath, then in vacuo. The liquid thus obtained is nearly pure bichlorhydrin; it begins to boil at 178°, and passes over constantly at that temperature to the end:

$$C^6H^8O^6 + 2HCl = C^6H^6Cl^2O^2 + 4HO;$$

Bichlorhydrin is also formed, though in small quantity, in the preparation of monochlorhydrin (p. 498); it is then found among the earlier portions of the distillate.

Neutral oil, having a very decided ethereal odour. Sp. gr. 1·37. Boils at 178°. Remains perfectly fluid at −35°.

				Berthelot.
6 C	36·0	28·0		27·6
6 H	6·0	4·7		5·0
2 Cl	70·8	54·9		53·7
2 O	16·0	12·4		13·7
$C^6H^6Cl^2O^2$	128·8	100·0		100·0

Primary nucleus C^6H^{10}; oxygen-nucleus $C^6H^8O^2$; chlorine-nucleus $C^6H^6Cl^2O^2$; — or primary nucleus C^6H^8; chlorine-nucleus $C^6H^6Cl^2$; bichlorhydrin = $C^6H^6Cl^2,O^2$.

Bichlorhydrin burns with a white green-edged flame, giving off hydrochloric acid. — When treated with potash, even in the cold, it soon deposits crystals of chloride of potassium. After a sufficiently prolonged reaction at 100° in a close vessel, the liquid no longer contains any substance soluble in ether. It contains a considerable quantity of chlorides, and if evaporated, after the addition of hydrochloric acid, forms a syrupy liquid, which, when treated successively with alcohol and oxide of silver, yields glycerine.

Bichlorhydrin mixes with ether, but does not form a stable emulsion with water (Berthelot, *N. Ann. Chim. Phys.* 41, 297).

Epichlorhydrin, $C^6H^5ClO^2$? — Formed by the action of hydrochloric acid upon bichlorydrin. 1. Several flasks of 1 litre capacity were

filled with dry hydrochloric acid gas; about a gramme of bichlorhydrin introduced into each; the flasks then sealed, and kept for 62 hours at 100°. The acid was then neutralized with potash, and the liquid distilled. The first portions of water that passed over were accompanied by a limpid liquid heavier than water, and having an ethereal odour just like that of hydrochloric ether, but more persistent. Sp. gr. between 1·2 and 1·3. — 2. A solution of bichlorhydrin in 15 to 20 times its weight of fuming hydrochloric acid was kept at a temperature of 100° for fifteen hours, this liquid then neutralized with lime, and distilled. An oil was thus obtained exactly resembling the preceding in odour and other properties; it distilled between 120° and 130°.

			Berthelot.	
			(1)	(2)
6 C	36·0	38·9	38·1	36·2
5 H	5·0	5·4	5·4	6·2
Cl	35·4	38·3		38·9
2 O	16·0	17·4		18·7
$C^6H^5ClO^2$	92·4	100·0		100·0

Primary nucleus C^6H^5; chlorine-nucleus $C^6H^5ClO^2$. — The formula of this body must not be regarded as definitely established, as it was probably not obtained in a state of purity. The formula agrees, however, with the results of the action of potash on the compound (*rid. inf.*) and with its comparatively low boiling point. For, chlorhydrin, $C^6H^7ClO^4$, boils at 227°, and epichlorhydrin, which differs from it by 2HO, boils at 120° or 130°. Now, according to VII, 61, the abstraction of 2HO lowers the boiling point of a compound by about 110°.

Epichlorhydrin (prepared by the second process), is decomposed by potash at 100°, yielding an alkaline liquid, which contains a considerable quantity of chlorides; does not give off inflammable vapours when boiled; gives up nothing to ether; and when treated successively with hydrochloric acid and absolute alcohol, yields a considerable quantity of a syrupy substance, which is deliquescent, nearly fixed, and similar to or identical with glycerine (Berthelot, *N. Ann. Chim. Phys.* 41, 299).

Iodhydrin. $C^{12}H^{11}IO^5$. — Obtained by saturating glycerine with hydriodic acid, keeping the liquid in a close vessel at 100° for forty hours, and then treating it with potash and ether:

$$2C^6H^8O^6 + HI = C^{12}H^{11}IO^5 + 6HO.$$

Syrupy liquid, which exhibits a golden iridescence, has a saccharine taste, is not volatile, but burns without residue, emitting vapours of iodine. Treated with potash at 100°, it is very slowly decomposed, yielding glycerine, iodide of potassium, and a liquid which is free from iodine, soluble in ether, volatilizes pretty easily, and is composed of $C^6H^5O^3 = C^6H^8O^6 - 3HO$.

Iodhydrin dissolves one-fifth of its volume of water. It is insoluble in water, but soluble in alcohol.

The iodine contained in cod-liver oil and other oils of like nature, may possibly be in the form of this or some similar compound (Berthelot & De Luca, *Compt. rend.* 39, 748).

Nitro-nucleus. $C^6H^5X^3O^4$.

¶ Nitroglycerine. $C^6N^3H^5O^{16}=C^6H^5X^3O^4$.

SOBRERO. *Compt. rend.* 24, 247.
R. RAILTON. *Chem. Soc. Qu. J.* 7, 222.

Discovered by Sobrero; more minutely investigated by Railton.

Formation. By the action of a mixture of strong nitric acid and oil of vitriol on glycerine at low temperatures (Sobrero, p. 488).

Preparation. Syrupy glycerine is slowly dropped into a mixture of equal volumes of strong nitric and sulphuric acids, kept cool by immersing the containing vessel in ice-cold water, the mixture being well shaken and cooled after each addition. The product which floats on the surface after a while, in the form of an oily liquid, is poured into cold distilled water, repeatedly washed with water by decantation, and afterwards freed as much as possible from the water by drying with blotting paper (Railton). — Sobrero used a mixture of 1 vol. nitric and 2 vol. oil of vitriol kept cool by a freezing mixture, and, after washing the product with water, dissolved it in alcohol and precipitated by water, or dissolved it in ether, and evaporated the ether, and afterwards dried the product in vacuo over oil of vitriol (p. 488). According to Railton, however, it cannot be dried in vacuo, as it is thereby rapidly decomposed.

Properties. Pale yellow liquid (Sobrero) heavier than water (Sobrero, Railton); inodorous, but has a sweet pungent and aromatic taste; and when placed upon the tongue, even in very small quantity, produces headache, which lasts for several hours (Sobrero).

Calculation, according to Railton.

6 C	36	.....	17·06
3 N	42	.....	19·91
5 H	5	.....	2·37
16 O	128	.....	60·66
$C^6H^5X^3O^4$	211	.....	100·00

Railton, by burning the substance with oxide of copper in a tube having metallic copper at its open end, obtained a mixture of 1 vol. N to 2 vol. CO^2, showing that it contains 1 At. N. to 2C, or 3N to 6C. The hydrogen could not be determined, in consequence of the impossibility of drying the substance completely.

Nitroglycerine boiled for some time with aqueous potash is decomposed, with formation of glycerine and nitrate of potash (Railton).

$$C^6H^5(NO^4)^3O^6 + 3(KO,HO) = C^6H^8O^5 + 3(KO,NO^5).$$

It is slightly soluble in *Water;* dissolves more readily in *Alcohol* and *Ether* (Railton) ¶.

Compounds probably formed from the nucleus $C^6N^4X^4H^4$.

1. Nitacrol.

REDTENBACHER. *Ann. Pharm.* 57, 145.
TILLEY. *Ann. Pharm.* 67, 106.

Choloïdic acid is distilled to one-fifth, with five times its volume of strong nitric acid; and in case red fumes are given off at the end of the process, the distillate is poured back, or fresh nitric acid added, and the distillation repeated till no more red vapours appear; the distillate then diluted with twice its bulk of water, again poured back, and redistilled. A crystalline, yellowish-white, thickish mixture of choloïdic, cholesteric, and oxalic acid then remains, and a colourless or brownish strongly acid watery distillate is obtained, having an intensely pungent and intoxicating odour, and below it, an oil having the same odour. The watery distillate is decanted from the heavy oil, and once more partially distilled, whereupon nitric oxide is given off, and a little more of the heavy oil passes over (the watery distillate contains acetic, cupric, caprylic, and perhaps also valerianic and butyric acids).

The whole of the heavy oil thus obtained, after being freed from adhering acids by washing with water, is colourless or pale yellow; much heavier than water; has an intensely pungent and intoxicating odour; excites tears, produces headache when inhaled; reddens litmus, dissolves sparingly in water, but readily in alcohol; and dissolves fats and soapy acids.

Decomposes at 100° with moderate detonation and bluish flame. — With aqueous potash, it is resolved into a yellow solution of *Nitrocholate of potash*, which, if the potash is sufficiently concentrated, separates out in yellow crystals,—and *Cholacrol*, which settles to the bottom in the form of an oil of different odour (Redtenbacher).

Nitacrol is also obtained, when œnanthyl is dropped into strong nitric acid, the mixture distilled, the distillate containing nitric acid, caproic acid, and nitacrol, diluted with water, and the drops of nitacrol which sink to the bottom, washed with water. — This also is a colourless oil, heavier than water, and having a sharp, penetrating odour which strongly irritates the mucous membrane of the nose. When heated to 100° in contact with water, it is resolved into nitrous acid and cholacrol; it likewise colours potash-solution intensely yellow, forming at the same time yellow crystals doubtless consisting of nitrocholate of potash, and a heavy transparent, and somewhat yellowish oil, the odour of which is nearly as intense as that of nitacrol, but in the dilute state resembles that of cinnamon. — Many other organic compounds appear also to yield nitacrol when heated with nitric acid, inasmuch as the resulting distillate assumes a yellow colour when treated with potash (Tilley).

2. Nitrocholic Acid. $C^6N^3H^4O^{22}=C^6N^4X^4H^4,O^6$?

REDTENBACHER. *Ann. Pharm.* 57, 145.

Nitrocholate of Potash. — Nitacrol is left for several days in contact with cold dilute potash, and the mixture frequently shaken; the yellow solution decanted from the cholacrol produced at the same time, and evaporated to the crystallizing point at a very gentle heat, or better, over oil of vitriol at ordinary temperatures. (The yellow mother-liquor, which yields no more crystals, smells like butter, and, when treated with dilute sulphuric acid, gives off nitrous fumes, then emits an odour of hydrocyanic acid and yields drops of oil smelling like fat, which rise to the surface. Alcohol likewise extracts from this mother-liquor a potash-salt containing a volatile soapy acid. — The preparation of nitrocholate of potash sometimes fails, the potash-solution assuming indeed a yellow colour when it first comes in contact with the nitracrol, but afterwards becoming suddenly violet-coloured, and yielding by evaporation, rose-coloured and violet crystals of another potash-salt, while the mother-liquor contains a large quantity of hydrocyanic acid).

The crystals of nitrocholate of potash, purified by solution in water and slow evaporation, are of the size of peas, apparently of the form of ferrocyanide of potassium, lemon-yellow, lustrous, and of slightly intoxicating odour. When dried in the air or in vacuo, and more quickly when heated, they burst into numerous fragments, which are scattered about, diffusing a powerful odour; the crystals at 100°. Their aqueous solution, when boiled for some time, yields nitrate of potash. Dilute sulphuric acid added to the solution of these crystals (or to the mother-liquor) separates nitrous, nitric, and hydrocyanic acid, and a fatty oil which rises to the surface (Redtenbacher).

Calculation according to Gm.			Calculation acc. to Redtenbacher.			Redtenb.
2 KO	94·4	23·34	KO	47·2	25·08	24·78
6 C	36·0	8·90	2 C	12·0	6·37	7·91
8 N	112·0	27·70	4 N	56·0	29·76	29·98
2 H	2·0	0·50	H	1·0	0·53	0·59
20 O	160·0	39·56	9 O	72·0	38·26	36·74
$C^6N^4X^4H^2K^2O^6$	404·4	100·00		188·2	100·00	100·00

The crystals with which the analysis was made were freed from the mother-liquor by pressure between paper.

3. Cholacrol.

REDTENBACHER. *Ann. Pharm.* 57, 145.

The heavy oil which separates out when nitacrol is treated with aqueous potash (p. 502). It is afterwards washed with water till it becomes neutral.

Pale yellow oil, heavier than water, and having a pungent, intoxicating, cinnamon-like odour. Neutral.

Decomposes at 100°, with evolution of nitrous fumes, sometimes also with slight detonation and emission of light, whilst a small quantity of liquid having a fatty odour remains behind.

Dissolves sparingly in water, not very abundantly in acids or alkalis, but readily in alcohol and ether (Redtenbacher).

	Dried over chloride of calcium.			Redtenbacher.
8 C	48	....	25·94	..... 26·15
2 N	28	....	15·14	..... 15·28
5 H	5	....	2·70	..... 2·81
13 O	104	....	56·22	..... 55·76
$C^8N^2H^5O^{13}$	185	....	100·00	..... 100·00

[Redtenbacher's formula certainly agrees closely with the analysis, but it is very improbable].

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Nitrite of Methyl. C^2H^3O,NO^3. — Obtained: 1. By treating wood-spirit with a mixture of nitric and arsenious acids. — 2. By the action of nitric acid on brucine:

$$\underbrace{C^{46}H^{26}N^2O^8}_{\text{Brucine.}} + 5(NO^5,HO) = \underbrace{C^2H^3O,NO^3}_{\text{Nitrite of methyl.}} + \underbrace{C^4H^{22}N^4O^{18}}_{\text{Cacotheline.}} + \underbrace{C^4H^2O^8}_{\text{Oxalic acid.}} + 2NO^2 + 4HO.$$

Very volatile, boiling at $-12{\cdot}5°$; has an odour like that of nitrous ether, and burns with a pale flame slightly tinged with green. With alcoholic potash, it yields nitrite of potash. Vapour-density = 0·991 (Strecker, *Ann. Pharm.* 91, 81; abstr. *Compt. rend.* 39, 49; *Chem Soc. Qu. J.* 7, 274).

Page 320.

Trimethylamine. — The hydriodate of this base is obtained by the action of iodide of methyl on aldehyde-ammonia. On mixing a clear solution of aldehyde-ammonia in a small quantity of alcohol with excess of iodide of methyl, needle-shaped crystals are formed in a few hours even at ordinary temperatures, the liquid at the same time becoming continually darker in colour; the action is complete in 24 hours. — The crystals are colourless and soluble in water. Heated on platinum foil, they are decomposed, with separation of charcoal. They emit an ammoniacal odour when heated with potash or lime; and their solution mixed with nitrate of silver yields a copious precipitate of iodide of silver (Man Saenz Diez, *Ann. Pharm.* 90, 299).

				Saenz Diez.
6 C	36	....	19·35	..... 18·63
10 H	10	....	5·38	..... 5·44
N	14	....	7·53	
I	126	....	67·74	..... 68·27
$(C^2H^3)^3N,HI$	186	....	100·00	

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Stannmethyl. C^2H^3Sn. — Formed by the action of tin on iodide of methyl (Frankland; Cahours & Riche). When iodide of methyl and metallic tin are heated together in sealed glass tubes to a temperature between 150° and 180°, the action is complete in the course of 15 to 20 hours, and the liquid contained in the tubes solidifies on cooling. The mass when distilled yields, first, from 195° upwards, a colourless, strong-smelling liquid, which does not solidify at 0°, — then, between 220° and 225°, the greater portion of the volatile product, amounting to $\frac{3}{4}$ of the substance used. This latter portion solidifies on cooling in a crystalline mass which, when fused, partially solidified, and separated by decantation from the remaining fluid portion, yields beautiful oblique rhombic prisms of *iodide of stannmethyl*, C^2H^3Sn,I, melting at 34°, moderately soluble in water, more soluble in alcohol, but dissolving in ether in all proportions. Ammonia added to the aqueous solution throws down *oxide of stannmethyl* as a white amorphous precipitate, which is soluble in excess of potash, insoluble in alcohol and ether, and dissolves in acids, forming crystallizable salts: *e. g.*, the *chloride* $=C^2H^3Sn,Cl$; the *sulphate* $=C^2H^3SnO,SO^3$, &c. (Cahours & Riche, *Compt. rend.* 26, 1001; *Ann. Pharm.* 88, 316; *Jahresber.* 1853, 48, 2). The salts are isomorphous with those of stannethyl (Frankland). — The pungent-smelling liquid formed simultaneously with iodide of stannmethyl, and boiling at about 200°, is the iodide of a radical polymeric with stannmethyl $=(C^2H^3)^2Sn^2,I$; when treated with ammonia, it yields an oxide which likewise forms crystallizable salts with acids (Cahours & Riche).

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Chloroform. — From experiments by A. Gunther, it appears that commercial chloroform is sometimes contaminated with Dutch liquid $C^4H^4Cl^2$; a sample treated with alcoholic potash for the preparation of formic acid, yielded a considerable quantity of gaseous chloride of acetyl, C^4H^3Cl, which is known to be formed by the action of alcoholic potash on Dutch liquid (p. 191 of this volume) but is not produced from pure chloroform under similar circumstances (Wöhler, *Ann. Pharm.* 91, 127).

Page 429.

Hydroferrocyanic acid. A cold-saturated solution of ferrocyanide of potassium mixed in small portions with an equal volume of hydrochloric acid free from iron, yields a snow-white, crystalline precipitate of pure hydroferrocyanic acid, which may be washed without loss with hydrochloric acid. After drying in a tube, it may be dissolved in alcohol, and crystallized out by covering the solution with a stratum of ether. (Liebig, *Ann. Pharm.* 87, 127).

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Cyanide of Cadmium. — According to E. Schüler (*Ann. Pharm.* 87, 46; *Jahresber.* 1853, 404); pure aqueous cyanide of potassium added to a perfectly neutral and not too dilute solution of chloride of cadmium, yields a bulky white precipitate of cyanide of cadmium, CdCy, soluble in excess of cyanide of potassium. The washed precipitate is an amorphous powder, which is permanent in the air at ordinary temperatures, but when heated in an open vessel turns brown and afterwards black, and forms a brown deposit of cadmic oxide; heated in a glass tube, it does not give off water or form cadmic oxide; but covers the tube with a specular deposit of cadmium. Hydrochloric acid dissolves it with evolution of hydrocyanic acid. — Contains 68·1 p.c. cadmium.

ADDITIONS TO VOL. VIII.

Page 7.

Cyanides of Copper and Cadmium. — *a.* $2CdCy,Cu^2Cy$. — Recently precipitated cadmic hydrate dissolves very slowly in excess of hydrocyanic acid, but quickly, and with evolution of carbonic acid and cyanogen, on the addition of recently precipitated cupric carbonate. If the addition of the latter substance be discontinued before the oxide of cadmium is completely dissolved, there remains a lavender-blue residue, which dissolves partially in boiling water (leaving pure oxide of cadmium) and forms a liquid, which soon becomes turbid and deposits a viscid milky substance, becoming crystalline as it cools, and apparently consisting of a mixture of two different salts. But if the addition of carbonate of copper be continued till the cadmic oxide is completely dissolved, a liquid is obtained which is colourless at first, but afterwards assumes a purple red colour, gradually in the cold, more quickly at 20° to 25°, and after being concentrated at 100°, soon deposits crystals of a dingy brown-red colour. The latter compound is sparingly soluble in cold water. From the solution in a small quantity of boiling water, it separates in the form of a red tenacious mass, which gradually solidifies to a net-work of crystals; but when recrystallized from a large quantity of boiling water, it forms shining, rose-coloured, oblique rhombic prisms, which are permanent in the air, and are not decomposed at 150°, but at higher temperatures become opaque, fuse, and quickly decompose (Schüler, *Ann. Pharm.* 87, 48).

	Dried at 100°.			Schüler (*mean*).
2 Cd	112	....	44·1	..... 45·5
2 Cu	64	....	25·2	..... 24·5
3 Cy	78	....	30·7	
$2CdCy,Cu^2Cy$	254	....	100·0	

b. $2CdCy,CuCy$. — When cadmic hydrate and cupric hydrate are dissolved together in hydrocyanic acid, and the colourless solution left to evaporate in the air, colourless, shining, oblique, rhombic prisms are obtained, which at 100° give off 18·4 p.c. of their weight, and crumble to a fine mealy powder. The salt is readily decomposed by acids. Both this and the preceding have a decided alkaline reaction and a peculiar metallic taste, leaving an irritating sensation in the throat (Schüler, *Ann. Pharm.* 87, 52).

				Schüler (*mean*).
2 Cd	112	....	50·4	..... 50·0
Cu	32	....	13·9	..... 14·1
3 Cy	78	....	35·7	
$2CdCy,CuCy$	222	....	100·0	

Page 25.

Cyanide of Mercury and Cadmium. 2CdCy,3HgCy. — A solution of cadmic hydrate and mercuric oxide in hydrocyanic acid, yields white opaque rectangular prisms, permanent in the air and readily soluble in cold water (Schüler, *Ann. Pharm.* 87, 54).

2 Cd	112	....	20·4	.....	19·5
3 Hg	300	....	55·2	.....	56·1
5 Cy	130	....	24·4		
2CdCy,3HgCy	542	....	100·0		

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Sulphocyanides of Platinum.

G. B. Buckton. *Chem. Soc. Qu. J.* 7, 22.

Sulphocyanide of platinum forms two series of salts analogous to the chloroplatinites and chloroplatinates, viz., the *Sulphocyanoplatinites* or *Platino-bisulphocyanides* $= C^4N^2MPtS^4 = MPt(CyS^2)^2 = MCyS^2 + PtCyS^2$, and the *Sulphocyanoplatinates* or *Platino-tersulphocyanides* $= C^6N^3MPtS^6 = MPt(CyS^2)^3 = MCyS^2 + Pt(CyS^2)^2$. — The potassium-salts of these two series are formed by the action of sulphocyanide of platinum on protochloride or bichloride of platinum respectively. All the salts are strongly coloured, exhibiting all shades of colour from light yellow to deep red. They are quickly decomposed by heat, emitting a peculiar odour. — When a salt of either series is treated with chlorine or nitric acid, it is decomposed, with formation of sulphuric and hydrocyanic acid, and deposition of a red or brown non-crystalline substance, which is insoluble in water and in alcohol, is not attacked by potash, but is coloured yellow by ammonia. This substance appears to be *platinous sulphocyanide*, $PtCyS^2$; its analysis gave 8·53 and 8·72 p.c. C, 9·92 N, 18·77 S, 62·27 and 62·02 Pt, besides 0·39 and 0·15 H, — calculation requiring 7·64 C, 8·93 N, 20·38 S, and 63·05 Pt. Its formation by the action of chlorine on sulphocyanoplanate of potassium may be represented by the equation:

$$KPt(CyS^2)^3 + 11Cl + 16HO = PtCyS^2 + KH(SO^4)^2 + 2HSO^4 + 11HCl + 2HCy.$$

Ammonia attacks the salts of both series, forming sulphocyanide of platosammonium (p. 515).

The following table exhibits the reactions of the two series of salts with various metallic solutions:

Reagents.	Sulphocyanoplatinites.	Sulphocyanoplatinates.
Neutral Lead salts	No change	Soluble golden laminæ
Basic Lead salts	Pale yellow precipitate	Fine red precipitate
Ferrous salts	No change	Black shining grains
Cobalt salts	No change	Orange-red precipitate
Cuprous salts	Purplish-black precipitate	Rich brown precipitate
Cupric salts	Purplish-black precipitate	Brick-red precipitate
Mercurous salts	No precipitate: liquid changes colour when heated	Orange precipitate
Silver salts	Pale yellow precipitate	Red or orange precipitate
Auric salts	Salmon-coloured precipitate	Salmon-coloured precipitate
Salts of Platosamine	Fine yellow precipitate	Copious orange precipitate
Salts of Diplatosamine	Flesh-coloured precipitate	Fine vermillion-red precipitate
Chromic acid	Copious reddish precipitate, with evolution of hydrocyanic acid	No precipitate
Ferrocyanide of potassium	Nearly white precipitate on boiling	Prussian blue formed on boiling

1. *Sulphocyanoplatinites.* $MPt(CyS^2)^2$.

Sulphocyanoplatinous acid. $HPt(CyS^2)^2$. — Obtained by cautiously decomposing sulphocyanoplatinite of barium with dilute sulphuric acid. The aqueous solution is speedily decomposed by evaporation, even in vacuo, the sulphur being oxidized at the expense of the water. The chief products of the decomposition are hydrosulphocyanic acid and a red or yellow deposit, rich in platinum.

Sulphocyanoplatinite of Potassium. — Obtained: 1. By dissolving protochloride of platinum in sulphocyanide of potassium, the solution being attended with considerable rise of temperature. — 2. Better, by the action of sulphocyanide of potassium on chloroplatinite of potassium, the sulphocyanide being in excess (VI, 322). As sulphocyanoplatinite of potassium is extremely soluble, and does not crystallize well by evaporation, it is best to use the sulphocyanide of potassium in the form of a concentrated solution, and to add the platinum-salt by small quantities at a time, so as to avoid too great a rise of temperature. The liquid on cooling deposits a mass of small needles, which must be purified from chloride of potassium by solution in strong alcohol, from which again the salt is best recovered by spontaneous evaporation. The crystals are then pressed between paper to remove the excess of sulphocyanide of potassium, and the salt once more crystallized from an aqueous solution.

Stellar groups of crystals, which, when examined by the microscope, appear like six-sided prisms of a fine red colour. They dissolve readily in $2\frac{1}{2}$ pts. of water at 15·5°, and are soluble to any extent in warm alcohol. The solution of the pure salt is orange-red; a port-wine colour denotes impurity. The crystals are not deliquescent, and when perfectly dry, do not appear to be affected by a temperature of 100°. — The salt is decomposed by ammonia, yielding sulphocyanide of platosammonium,

which crystallizes out, and sulphocyanide of potassium which remains in solution (p. 515).

	Crystals dried over oil of vitriol.			Buckton.
4 C	24	....	9·44	..... 9·34
2 N	28	....	11·02	..... 10·66
4 S	64	....	25·18	..... 25·44
K	39	....	15·38	..... 15·27
Pt	99	....	38·98	..... 38·78
$KPt(CyS^2)^2$	254	....	100·00	..... 99·49

Sulphocyanoplatinite of Silver. Curdy precipitate, somewhat resembling sulphocyanide of silver, partially soluble in ammonia, with decomposition. Dissolves in sulphocyanide of potassium, but the solution is decomposed by water.

				Buckton (*mean*).
2 N	28	....	8·66	..... 8·53
4 S	64	....	19·81	..... 19·40
Ag	108	....	64·08	..... 63·98
Pt	99			
4 C	24	....	7·45	..... 6·94
$AgPt(CyS^2)^2$	323	....	100·00	

Sulphocyanoplatinite of Diplatosammonium. — Obtained, as a bulky flesh-coloured precipitate, by decomposing the chloride of diplatosammonium with a soluble sulphocyanoplatinite. — Heated on platinum-foil, it gives off ammoniacal gas, fuses into a black bubbling mass, and then burns like tinder, leaving bright spongy platinum. It is quite insoluble in water and in alcohol, but dilute hydrochloric acid dissolves it rather freely.

				Buckton (*mean*).
4 C	24	....	6·90	..... 6·65
6 H	6	....	1·72	..... 1·19
4 N	56	....	16·09	
4 S	64	....	18·39	..... 18·62
2 Pt	198	....	56·90	..... 56·94
$PtH^6N^2,Pt,(CyS^2)^2$	348	....	100·00	

Polymeric with sulphocyanide of platosammonium (p. 516).

2. *Sulphocyanoplatinates.* $MPt(CyS^2)^2$.

Sulphocyanoplatinic Acid. $HPt(CyS^2)^2$. — Obtained by precipitating a warm and concentrated solution of the lead-salt with sulphuric acid. The filtered liquid is of a deep-red colour, and has a strongly acid taste. It displaces carbonic acid from its combination with the alkalis, and dissolves metallic zinc, with evolution of hydrogen and production of a yellow insoluble substance. When rapidly evaporated in vacuo, it leaves a confused semi-crystalline mass. When concentrated over the water-bath, it is quickly decomposed, leaving a brown amorphous mass rich in

platinum. On distilling it at a gentle heat, an acid liquid passes over containing hydrocyanic and hydrosulphocyanic acids. It combines directly with bases.

Sulphocyanoplatinate of Ammonium. — The acid does not combine rapidly with free ammonia; but the salt is easily prepared by boiling 1 pt. of sulphate of ammonia for a few minutes in a strong solution of 3·5 pts. of sulphocyanoplatinate of potassium; it may be separated after cooling, from the sulphates of ammonia and potash by means of alcohol, and purified by recrystallization from hot water. Crystallizes in hexagonal plates of a fine crimson colour. It is stable at ordinary temperatures, but gives off the odour of sulphocyanic acid when its aqueous solution is boiled.

				Buckton.
6 C	36	....	12·37	..... 12·14
4 H	4	....	1·38	..... 1·56
4 N	56	....	19·24	
6 S	96	....	32·99	
Pt	99	....	34·02	..... 34·17
$NH^4Pt(CyS^2)^3$	291	....	100·00	

Sulphocyanoplatinate of Potassium. — *Preparation.* 1. By the action of sulphocyanide of potassium on bichloride of platinum. When bichloride of platinum is added to a cold solution of sulphocyanide of potassium, a precipitate of chloroplatinate of potassium is formed, with evolution of hydrosulphocyanic acid. But if the bichloride of platinum be poured into a strong solution of sulphocyanide of potassium, previously heated to 70° or 80°, no precipitate is formed, but the liquor acquires a deep red colour, and on cooling deposits beautiful laminæ of sulphocyanoplatinate of potassium. This process involves a considerable waste of sulphocyanide of potassium, in consequence of the presence of free hydrochloric acid, which likewise, if the temperature rises above a certain point, decomposes the product, forming a brown flocculent precipitate (platinous sulphocyanide). — 2. Better: A solution of 4 pts. of chloroplatinate of potassium is added to a solution of 5 pts. of pure sulphocyanide of potassium (weighed in the fused state) in a moderate quantity of water, and the mixture heated nearly to the boiling point:

$$KPtCl^3 + 3KCyS^2 = KPt(CyS^2)^3 + 3KCl.$$

A deficiency of the sulphocyanide must be avoided, as in that case an insoluble brown substance is formed, which renders the purification of the crystals very difficult. The filtered liquid, on cooling, deposits the sulphocyanoplatinate in beautiful crystals, often of a large size. To remove traces of chloride of potassium, the crystals may be redissolved in boiling alcohol, and the solution passed through a filter surrounded with hot water, to prevent too rapid crystallization.

Properties. Six-sided prisms or laminæ, of a deep carmine colour, and very nauseous taste. The aqueous solution yields the salt in hexagonal plates; but from the alcoholic solution it is often deposited in double six-sided pyramids united base to base, with their apices truncated. Permanent in the air at ordinary temperatures. The solution has a deep red colour, becoming yellow when very dilute. One drop of the saturated solution gives a distinct yellow tinge to a gallon of water.

	Dried in vacuo over oil of vitriol.		Buckton (*mean*).
6 C	36	11·53	11·72
3 N	42	13·46	13·58
6 S	96	30·76	30·83
K	39	12·52	12·73
Pt	99	31·73	31·63
$KPt(CyS^2)^3$	312	100·00	100·29

Decompositions. 1. Sulphocyanoplatinate of potassium is decomposed at a red heat, yielding sulphocyanide of potassium, gaseous products, and reduced platinum. — 2. When gently heated in contact with the air, it burns with a blue sulphurous flame and peculiar odour. — 3. Hydrosulphuric acid converts it into hydrosulphocyanic acid, sulphocyanide of potassium, and bisulphide of platinum:

$$KPt(CyS^2)^3 + 2HS = PtS^2 + KCyS^2 + 2HCyS^2.$$

Similarly, with sulphide of ammonium:

$$KPt(CyS^2)^3 + 2NH^4S = PtS^2 + KCyS^2 + 2NH^4CyS^2.$$

By precipitating a solution of 0·715 grm. of the salt with sulphide of ammonium, heating the liquid on the water-bath till all traces of free ammonia had disappeared, then adding acetic acid, filtering from the bisulphide of platinum, and treating the clear liquid with nitrate of silver acidulated with a few drops of nitric acid to prevent the formation of acetate of silver, a precipitate of sulphocyanide of silver was obtained, weighing 1·127 grm. and equivalent to 0·3999 grm. or 55·90 per cent of sulphocyanogen: calculation requires 55·76. — 4. The salt is decomposed by strong sulphuric and hydrochloric acid. Nitric acid and chlorine likewise decompose it, yielding platinous sulphocyanide $PtCyS^2$, and other products (p. 509). — 5. Ammonia and carbonate of ammonia added to a saturated solution of the salt, quickly decompose it, changing the colour to pale yellow in a few minutes and precipitating *sulphocyanide of platosammonium* in fine yellow needles; the liquid retaining in solution sulphate of potash, sulphocyanide of potassium, sulphocyanide of ammonium and cyanide of ammonium:

$$6KPt(CyS^2)^3 + 8NH^3 + 8HO = 6NH^3PtCyS^2 + 2(KO,SO^3) + 4KCyS^2 + 2NH^4CyS^2 + 5HCyS^2 + HCy.$$

6. Potash converts the salt into a red, gelatinous mass, without evolution of ammonia. — 7. When it is gently heated with carbonate of potash, carbonic acid is evolved; the mixture becomes partially decolorized; sulphocyanoplatinite of potassium is deposited; and the liquid retains in solution, sulphate of potash, sulphocyanide of potassium, and cyanide of potassium:

$$6KPt(CyS^2)^3 + 8(KO,CO^2) = 6KPt(CyS^2)^2 + 2(KO,SO^3) + 5KCyS^2 + KCy + 8CO^2.$$

8. A pure solution of sulphocyanoplatinate of potassium does not produce a blood-red colour with ferric salts; but the mixture becomes nearly black and opaque when heated, from formation of a substance in heavy lustrous grains.

Combinations. Dissolves in 12 pts. of *Water* at 60°, C; but is much more soluble in boiling water, and still more in boiling *Alcohol.*

Sulphocyanoplatinate of Sodium. — Obtained by precipitating the lead-salt with sulphate of soda. Crystallizes readily in broad garnet-coloured tables, soluble in water and in alcohol.

Sulphocyanoplatinate of Barium. — Prepared by dissolving 3 pts. of the dry potassium-salt in an aqueous solution of 1 pt. of chloride of barium (or as an excess of the latter is desirable, 9 pts. $KPt(CyS^2)^3$ to 4 pts. BaCl), evaporating the solution, and extracting with alcohol. — Crystallizes in long flattened prisms of a deep red colour, and often of considerable size. Not so stable as the potassium-salt.

Sulphocyanoplatinate of Lead. — *a. Basic.* $PbO,PbPt(CyS^2)^3$. — Obtained as a brilliant red precipitate on mixing the concentrated solutions of sulphocyanoplatinate of potassium and basic acetate of lead. Insoluble in water; readily soluble in dilute nitric and in acetic acid.

				Buckton.
6 C	36	....	7·49	
3 N	42	....	8·73	
6 S	96	....	19·96	
2 Pb	208	....	43·24	..... 43·46
Pt	99	....	20·58	
$PbO,PbPt(CyS^2)^3$	481	....	100·00	

b. Neutral. $PbPt(CyS^2)^3$. — Precipitated in the form of brilliant golden hexagonal plates, on mixing the concentrated solutions of neutral acetate of lead and sulphocyanoplatinate of potassium. Soluble in alcohol; less soluble in cold water, with which it may be washed; cannot be crystallized from hot water without decomposition.

Ferrous Sulphocyanoplatinate. — Obtained by adding a slightly acidulated solution of ferrous sulphate to a concentrated solution of sulphocyanoplatinate of potassium. Black, crystalline precipitate, which, when examined by the microscope, is seen to be composed of shining six-sided laminæ with rounded edges. It is not affected by dilute sulphuric, hydrochloric, or nitric acid; but strong nitric acid dissolves it, with formation of sulphuric acid. Cold solution of potash converts it into ferric oxide and a yellow liquid containing platinum and sulphocyanogen. It is insoluble in water and in alcohol.

				Buckton (*mean*).
6 C	36	....	11·96	..... 11·73
3 N	42	....	13·95	..... 13·73
6 S	96	....	31·89	..... 32·08
Fe	28	....	9·30	..... 9·28
Pt	99	....	32·90	..... 33·23
$FePt(CyS^2)^3$	301	....	100·00	100·07

Ferric Sulphocyanoplatinate. — Prepared in like manner with a ferric salt, but is not precipitated till the mixture is boiled. Resembles the ferrous salt.

Cupric Sulphocyanoplatinate. — Precipitated on mixing a solution of the potassium-salt with cupric sulphate. Exhibits a brick-dust red colour when first precipitated, but changes at a boiling heat to a black insoluble powder. Forms a fine green solution with ammonia, but on the addition of hydrochloric acid, the copper-salt is reproduced, with dark brown colour.

Mercurous Sulphocyanoplatinate. — Heavy curdy precipitate, obtained by adding mercurous nitrate to sulphocyanoplatinate of potassium. Its colour is deep orange at first, but changes to a pale primrose-yellow, when the liquid is heated to the boiling point.

				Buckton (*mean*).
6 C	36	....	7·61	..... 7·68
3 N	42	....	8·87	
6 S	96	....	20·29	
2 Hg	200	....	42·28	
Pt	99	....	20·95	..... 21·04
$Hg^2Pt(CyS^2)^3$	473	....	100·00	

Mercurous sulphocyanoplatinate, in the dry state, bears a considerable degree of heat without alteration. Heated in the air-bath to between 140° and 150°, it suddenly swells up into a substance having a peculiar metallic and arborescent appearance, somewhat like coarse tea, and emits a jet of spontaneously inflammable gas. The arborescent substance contains 23·49 per cent of platinum. No further change is observed till the temperature rises to 250°; but at a heat below redness, mercurial vapours and cyanogen gas are liberated; and finally, the mass, if exposed in an open crucible, burns away like tinder, leaving a residue of platinum. The salt, when subjected to dry distillation in a retort, yields a mixture of nitrogen gas and vapour of bisulphide of carbon.

Sulphocyanoplatinate of Silver. — Prepared by decomposing a solution of the potassium-salt with nitrate of silver. Heavy, curdy, deep orange-coloured precipitate, which shrinks and agglutinates into a tenacious mass when boiled with water, but hardens again on cooling.

				Buckton.
6 C	36	....	9·44	..... 9·10
3 N	42	....	11·12	
6 S	96	....	25·11	
Ag	108	....	54·33	..... 54·32
Pt	99			
$AgPt(CyS^2)^3$	381	....	100·00	

The dry salt, when gently heated, swells up considerably, and if in contact with the air, takes fire and burns with a blue flame. Before the blowpipe, it fuses into a metallic bead of silver and platinum. — Nitric acid decomposes it rapidly, with formation of sulphuric acid, evolution of nitric oxide, and precipitation of a yellow substance. — When recently precipitated, it dissolves in cold ammonia, but the solution decomposes at a higher temperature. The salt is decomposed by hot caustic potash, yielding sulphocyanide of potassium, binoxide of platinum, and oxide of silver:

$$AgPt(CyS^2)^3 + 3KO = 3KCyS^2 + PtO^2 + AgO.$$

It dissolves in sulphocyanide of potassium, but on adding water to the solution, sulphocyanide of silver is precipitated, and sulphocyanoplatinate of potassium remains in solution:

$$AgPt(CyS^2)^3 + KCyS^2 = AgCyS^2 + KPt(CyS^2)^3.$$

Sulphocyanide of Platosammonium. — $C^2H^3N^2S^2Pt = NH^3Pt,CyS^2$. — Obtained: 1. By the action of ammonia on sulphocyanoplatinite of potassium:

$$KPt(CyS^2)^2 + NH^3 = NH^3Pt,CyS^2 + KCyS^2.$$

2. By the action of ammonia or carbonate of ammonia on sulphocyano-

platinate of potassium. (For the equation, *vid.* p. 513). Caustic ammonia acts more quickly than the carbonate, but must not be used in the concentrated state, as the product is then contaminated with an insoluble substance. The crystals are collected on a filter, washed with cold water, and recrystallized from hot alcohol. — 3. By double decomposition with sulphocyanide of potassium and chloride of platosammonium :

$$NH^3Pt,Cl + KCyS^2 = NH^3Pt,CyS^2 + KCl.$$

1 pt. of sulphocyanide of potassium and 1·6 pt. of chloride of platosammonium are dissolved together in water; the mixture heated nearly to its boiling point ; an equal volume of alcohol added to increase the solubility of the product ; and the liquid filtered hot. Sulphocyanide of platosammonium is then deposited in crystals on cooling.

Straw-yellow needles, which, when examined by the microscope, appear to be rhomboïdal prisms. Melts between 100° and 110°, to a clear garnet-coloured syrup, which hardens again as it cools.

				Buckton.	
2 C	12	....	6·89	.....	6·69	
2 N	28	....	16·09	.....	15·89	
3 H	3	....	1·74	.....	1·81	
2 S	32	....	18·39	.....	18·55	
Pt	99	....	56·89	.....	56·74	..... 56·68
NH^3Pt,CyS^2	174	....	100·00	.....	99·68	

Polymeric and metameric with sulphocyanoplatinite of diplatosammonium (p. 511) $2(NH^3Pt,CyS^2) = [NH^2Pt(NH^4)],Pt,(CyS^2)^2$.

Decomposes at 180°, giving off ammonia and hydrocyanic acid, and if exposed to the air, evolves also sulphurous acid and leaves metallic platinum ; no sulphide of carbon is given off. It is not attacked by hydrochloric or by dilute sulphuric acid. — The aqueous solution produces no change in salts of copper, lead, or mercury ; but when added to a solution of sulphate or nitrate of silver, it forms a light yellow precipitate containing platinum. When boiled, it gives off ammonia, and deposits the yellow insoluble matter above mentioned ; the same effect appears to be produced by caustic potash.

The salt dissolves sparingly in cold water, more readily in alcohol.

Page 109.

Pseudosulphocyanogen. — Völckel (*Ann. Pharm.* 89, 125) has re-examined the yellow substance precipitated by chlorine from solutions of the sulphocyanides. Jamieson, by analyzing a specimen which had been boiled with water for a long time, obtained results from which he deduced the formula $C^4N^2HS^4,HO$. Völckel observed that, when the yellow substance was boiled with water, it yielded small quantities of hydrosulphocyanic acid, sulphuretted hydrogen, and a yellow sulphuretted body soluble in water. The pseudosulphocyanogen at the same time became somewhat darker in colour, and gave by analysis numbers agreeing with Jamieson's formula. But when pseudosulphocyanogen which had not been boiled with water was dissolved, after perfect desiccation, in strong *sulphuric* acid, the yellow solution precipitated by water, and the sepa-

rated yellow flocks washed with cold water and thoroughly boiled with absolute alcohol, the product thus purified yielded numbers corresponding with the formula $C^4N^2HS^4$, proposed by Laurent & Gerhardt.

				Völckel.	
4 C	24	20·51	20·20		20·31
2 N	28	23·93			
H	1	0·85	0·90		0·91
4 S	64	54·71			
$C^4N^2HS^4$	117	100·00			

It appears then that the additional HO found by Jamieson was due to the boiling with water, and that pseudosulphocyanogen is formed from hydrosulphocyanic acid by abstraction of hydrogen:

$$2C^2NHS^2 + Cl = C^4N^2HS^4 + HCl.$$

Page 127.

Nitroprussides. — E. W. Davy has discovered for these compounds the following modes of formation, in addition to those given by Playfair: 1. By the action of $3\frac{1}{2}$ pts. hydrochloric acid diluted with twice its bulk of water on a mixture of 1 pt. ferrocyanide of potassium and 2 or 3 parts of chlorate of potash, at ordinary temperatures. — 2. By the action of an aqueous solution of hypochlorous acid on ferrocyanide of potassium at 33° to 43°. — 3. By exposing an aqueous solution of ferrocyanide of potassium and chlorate of potash to sunshine. The action does not take place in the dark (*Phil. Mag. J*, [4], 6, 11).

Page 130.

Nitroprusside of Potassium. — This salt may be conveniently prepared by neutralizing with carbonate of potash the liquid obtained by decomposing ferrocyanide of potassium with nitric acid, evaporating nearly to dryness, exhausting the residue with alcohol, or better with ether and alcohol, and leaving the solution to evaporate. The salt separates in ruby-coloured prisms, which, by one recrystallization, may be obtained nearly pure (J. B. Enz, *Vierteljahresber. pr. Pharm.* 2, 239 ; *Jahresber.* 1853. 406).

Page 163.

Olefiant gas. — The intumescence which causes so much inconvenience in the preparation of this gas with alcohol and oil of vitriol, may be completely prevented by adding to the mixture a sufficient quantity of sand to form a thick, scarcely fluid mass. When such a mixture is heated, scarcely any frothing takes place; the decomposition may be carried almost to the end; and nearly all the carbon of the alcohol is obtained in the form of olefiant gas. 50 grammes of 80 p.c. spirit thus treated, yielded 22 litres of gas (Wöhler, *Ann. Pharm.* 91, 127).

Page 172.

Oxide of Ethyl. — May be obtained by the action of hydrobromic ether on an alcoholic solution of potash, the two liquids being enclosed in a sealed tube, and exposed for eight hours to a temperature of 100°:

$$C^4H^5Br + KO + C^4H^6O^2 = C^8H^{10}O^2 + KBr + HO.$$

The reaction thus considered is analogous to that of iodide of ethyl on potassium-alcohol (VIII, 172). The formation of the ether might, however, be represented by the simpler equation:

$$C^4H^5Br + KO = C^4H^5O + KBr,$$

the alcohol being supposed not to take a direct part in the decomposition, but merely to act as a solvent. In this case, however, 1 At. C^4H^5Br should produce 1 At. ether = C^4H^5O, and the quantity of alcohol used would be indifferent; whereas, according to the former equation, 1 At. C^4H^5Br should produce 1 At. ether = $C^8H^{10}O^2 = 2C^4H^5O$, that is to say, twice as much as on the other hypothesis, and the quantity of alcohol required should be just 1 At. Moreover, if the decomposition takes place according to the first equation, we ought, by using wood-spirit instead of alcohol, to obtain vinomethylic ether. To decide this point, the following experiments were made:

a. 22 grm. hydrobromic ether, heated to 100° for six hours with 15 grm. of potash and 12 grm. absolute alcohol, yielded 12 grm. of oxide of ethyl. According to the first of the above equations, the quantity obtained should be 15 grm.; according to the second, only 7½. The result approaches as near to the former quantity as can be expected in an experiment of this nature, and shows that the alcohol is really concerned in the reaction.

b. 6 grm. of hydrobromic ether were heated to 100° for six hours with an excess of potash and 2 grm. of absolute alcohol, the equivalent quantity being 2½ grm. The decomposition was incomplete, the product being a mixture of common ether and bromide of ethyl.

c. Hydrobromic ether heated with potash and wood-spirit, yielded vinomethylic ether (Berthelot, *N. J. Pharm.* xxvi. 25).

Page 195.

Formation of Alcohol from Ether. — Common ether heated to 360° in close vessels with benzoic, butyric, or palmitic acid, combines with the acids, forming benzoic, butyric, or palmitic ether; and these ethers, when decomposed by potash, yield alcohol (Berthelot, *N. J. Pharm.* 26, 28).

Page 274.

Aldehyde. — Völckel has found aldehyde among the products obtained by the dry distillation of sugar (*N. J. Pharm.* 26, 159).

Aldehyde-ammonia. — For the action of iodide of methyl on this compound, see page 505.

Page 393.

Carbonate of Ethyl.—May be obtained by the action of iodide of ethyl on carbonate of silver:

$$AgO,CO^2 + C^4H^5I = AgI + C^4H^5O,CO^2.$$

On mixing the two substances in equal weights, distilling when the mass has become dry and pulverulent, and rectifying at 126°, a product is obtained having the properties of carbonic ether, and yielding by analysis 50·5 p.c. C and 8·5 H (Ph. de Clermont, *Ann. Pharm.* 91, 376).

Page 398.

Phosphates of Ethyl.—The pyrophosphate and tribasic phosphate of ethyl are likewise obtained by the action of iodide of ethyl on the corresponding silver-salts.

a. Pyrrophosphate. — Pure dry iodide of ethyl is inclosed, together with perfectly dry pyrophosphate of silver, in a sealed flask, and the mixture heated in the water-bath. The mass is then treated with ether; the liquid filtered from the iodide of silver; the ether distilled off in the water-bath; and the viscid residue dried by passing air through it at 130°, and afterwards heating it to 140° in vacuo:

$$2AgO,PO^5 + 2C^4H^5I = 2AgI + 2C^4H^5O,PO^5.$$

Viscid liquid, of sp. gr. 1·172 at 17°; has a peculiar odour and burning taste. Burns, when heated, with a whitish flame, and diffuses white vapours. Potash decomposes it, with formation of a crystallizable, deliquescent salt (probably $2C^4H^5O,KO,PO^5$). It is soluble in water, alcohol, and ether; soon turns acid when exposed to the air (it absorbed 14 p.c. water in a few days); and dissolves a small quantity of iodide of silver (De Clermont).

				De Clermont.
8 C	48·0	33·0		33·7
10 H	10·0	6·9		6·7
2 O	16·0	11·0		10·3
PO^5	71·4	49·1		49·3
$2C^4H^5O,PO^5$	145·4	100·0		100·0

b. Tribasic Phosphate. — Iodide of ethyl acts but slightly on phosphate of silver at ordinary temperature, but completely at the heat of the water-bath. The mass is exhausted with ether; the liquid which remains after the evaporation of the ether, heated in an oil-bath to 160°, at which temperature it does not boil; and distilled in vacuo at 140°. (The liquid which remains at this temperature is very viscid and sour, and absorbs moisture rapidly from the air). The distillate is phosphate of ethyl.

Colourless liquid, which smells like the preceding compound; has a burning taste; forms an acid mixture with water; and burns, when heated with a white flame, emitting white fumes (De Clermont).

			De Clermont.
12 C	72·0	39·5	39·1
15 H	15·0	8·2	8·4
3 O	24·0	13·2	
PO^2	71·4	39·1	
$3C^2H^2O,PO^2$	182·4	100·0	

Pages 487 and 488.

Cyanate of Ethyl. — This liquid boils at 60°. Its specific gravity is 0·8981; Vapour-density = 2·475.

			Würtz.
6 C	36	50·70	50·35
5 H	5	7·04	7·26
N	14	19·72	19·89
2 O	16	22·54	
$C^2N(C^2H^5)O^2$	71	100·00	

The calculation of the composition on page 488, Vol. VIII, is incorrect, 6C having been inadvertently estimated at 24, instead of 36.

Cyanic ether when very pure does not decompose spontaneously, but may be kept unchanged in sealed tubes for years.

Cyanate of Methyl. — Obtained by distilling a mixture of 2 pts. sulphomethylate with 1 pt. cyanate of potash, the receiver being well cooled with a freezing mixture, and the uncondensed vapours passed, either into a chimney having a strong draught, or into a bottle containing a small quantity of caustic ammonia, and well cooled. The sulphomethylate of potash used in the preparation should be well crystallized in tables, and the crystals, which are anhydrous, carefully freed from mechanically enclosed water. The product of the operation is a mixture of liquid cyanate and crystallized cyanurate of methyl.

Cyanate of methyl, when rectified, is a light, colourless liquid, very mobile and volatile, boiling at about 40°. Its vapours are irritating and suffocating in the highest degree.

			Wurtz.
4 C	24	42·10	41·99 — 42·39
3 H	3	5·26	5·37 — 5·56
N	14	24·56	
2 O	16	28·08	
$C^2N(C^2H^3)O^2$	57	100·00	

Cyanate of methyl enclosed in a sealed tube and left to itself, is entirely transformed, in an interval of time varying from five minutes to fifteen days, into a crystalline mass of cyanurate; when the change takes place quickly, it is attended with perceptible rise of temperature. Its reactions are similar to those of the ethyl-compound. Potash transforms it into carbonic acid and methylamine; ammonia unites with it, forming methyl-urea; under the influence of water, it is resolved into carbonic acid and dimethyl-urea. (Wurtz *N. Ann. Chim. Phys.* 42, 61).

ADDITIONS TO VOL. IX.

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Ethylacetamide. — Obtained by the action of cyanic ether on an equal volume of glacial acetic acid. The liquids act upon each other at ordinary temperatures, carbonic acid being evolved; and, if a gentle heat be applied, the action is soon terminated, and there remains in the tube a liquid much less volatile than the original mixture. On distilling this liquid, the excess of acetic acid passes off first, and the temperature then rises rapidly to about 200°, at which point, ethylacetamide passes over in the form of a liquid perfectly neutral to test-paper.

Pure ethylacetamide boils at 205°. Its sp. gr. is 0·942 at 4·5°. It dissolves in all proportions in water and in alcohol, and is precipitated from its aqueous solution by potash in the cold, in the form of an oily liquid which floats on the alkaline solution (Wurtz, *N. Ann. Chim. Phys.* 42, 53).

				Wurtz.
8 C	48	....	55·11	54·70
9 H	9	....	10·34	10·22
N	14	....	16·09	16·10
2 O	16	....	18·46	
$N\begin{cases} H \\ C^4H^5 \\ C^4H^3O^2 \end{cases}$	87	....	100·00	

Ethylodiacetamide. — Prepared by heating a mixture of about equal volumes of anhydrous acetic acid (boiling at 137°) and cyanic ether to 180° —200°, in a very strong glass tube hermetically sealed. On opening the tube after cooling, a violent evolution of carbonic acid takes place, and the remaining brown liquid, when gently heated, gives off about 50 times its volume of that gas. On distilling this liquid, the boiling point rises rapidly to 185°, and the greater part of the liquid passes over at about 192°. — The distillate, which is ethylodiacetamide, is perfectly limpid and colourless; its density is 1·0092 at 20°. (Wurtz, *N. Ann. Chim. Phys.* 42, 45).

				Wurtz.
12 C	72	....	55·81	55·69
11 H	11	....	8·53	8·95
N	14	....	10·85	
2 O	32	....	24·81	
$N\begin{cases} C^4H^5 \\ C^4H^3O^2 \\ C^4H^3O^2 \end{cases}$	129	....	100·00	

Ethyloformiamide. $C^6H^7NO^2 = NH,(C^4H^5)C^2HO^2$. — Formed by the action of cyanic ether on monohydrated formic acid:

$$\left.\begin{matrix}C^2HO^2\\H\end{matrix}\right\}O^2 + \left.\begin{matrix}C^2N\\C^4H^5\end{matrix}\right\}O^2 = N\left\{\begin{matrix}H\\C^4H^5\\C^2HO^2\end{matrix}\right\} + 2CO^2$$

Pure formic acid, prepared by decomposing formiate of lead with sulphuretted hydrogen, and rectifying the product over an excess of formiate of lead, is mixed with cyanic ether. — Violent action immediately takes place, attended with rapid evolution of carbonic acid, which may be moderated by immersing the tube in ice-cold water. The evolution of gas then goes on for several hours; and when it is terminated, the tube is sealed and heated in the water-bath. On opening the tube after cooling, a final portion of carbonic acid escapes, and a colourless liquid is obtained containing an excess of cyanic ether. The greater part of this liquid passes over between 198° and 200°, and the product thus obtained is ethyloformiamide.

Transparent, colourless, neutral liquid, having a sweet taste. Sp. gr. 0·967 at 2°. Boils at 199°.

				Wurtz.
6 C	36	....	49·31	..... 49·55
7 H	7	....	9·45	..... 9·81
N	14	....	19·17	
2 O	16	....	22·07	
$N\left\{\begin{matrix}H\\C^4H^5\\C^2HO^2\end{matrix}\right.$	73	....	100·00	

Ethyloformiamide is decomposed by potash at a boiling heat, yielding formiate of potash and ethylamine.

$$N\left\{\begin{matrix}H\\C^4H^5\\C^2HO^2\end{matrix}\right. + \left.\begin{matrix}K\\H\end{matrix}\right\}O^2 = N\left\{\begin{matrix}H\\H\\C^4H^5\end{matrix}\right. + \left.\begin{matrix}C^2HO^2\\K\end{matrix}\right\}O^2.$$

It dissolves in all proportions in water and in alcohol (Wurtz, *N. Ann. Chim. Phys.* 42, 55).

Page 276.

Ethylurethane. $C^{10}H^{11}NO^4$. — Obtained by the action of cyanic ether upon alcohol:

$$C^6H^5NO^2 + C^4H^6O^2 = C^{10}H^{11}NO^4.$$

A mixture of the two liquids in about equal volumes is enclosed in a sealed tube of hard glass, and heated in the water-bath for a few hours. The resulting liquid mixed with water, yields an oily layer lighter than water which, when decanted and distilled, passes over for the most part, between 170° and 180°; and this distillate after several rectifications, yields ethylurethane in the form of an oily liquid, having an odour something like that of carbonic ether. — Sometimes, however, after the ethylurethane has distilled over, and the boiling point has risen to 180°, the small quantity of liquid remaining in the retort

solidifies on cooling in a crystalline mass, consisting of diethylurea, $C^{10}H^{12}N^2O^2$ (p. 291). The formation of this product is probably due to a secondary action, giving rise at the same time to the formation of a small quantity of carbonic ether: thus,

$$2C^6H^5NO^2 + 2C^4H^6O^2 = 2(C^4H^5O,CO^2) + C^{10}H^{12}N^2O^2.$$

Ethylurethane is sometimes obtained in the preparation of cyanic ether, probably in consequence of the cyanate of potash retaining a little alcohol.

Properties. — Ethereal liquid, having a peculiar odour, much like that of carbonic ether. Sp. gr. 0·9862 at 21°. Boils at 174° — 175°. Vapour-density 4·071.

				Wurtz.					
				a.	*b.*				
10 C	.....	60	.... 51·28	.... 51·34	.... 51·17	C-vapour	 10	....	4·1600
11 H	.....	11	.... 9·40	.... 9·70	.... 9·60	H-gas	 11	....	11·7623
N	.....	14	.... 11·96	.... 11·61	.... 12·16	N-gas	 1	....	0·9706
4 O	.....	32	.... 27·36	.... 28·35	.... 27·07	O-gas	 2	....	2·2186
$C^{10}H^{11}NO^4$		117	.... 100·00	.... 100·00	.... 100·00		2	....	8·1115
							1	....	4·0557

a is the mean of two analyses made with products obtained by the direct action of cyanic ether upon alcohol; *b*, the mean of two analyses made with products obtained in the preparation of cyanic ether.

Ethylurethane boiled with caustic potash is resolved into alcohol, ethylamine and carbonic acid:

$$C^{10}H^{11}NO^4 + 2(KO,HO) = C^4H^6O^2 + C^4H^7N + 2(KO,CO^2).$$

It mixes with sulphuric acid at ordinary temperatures, without decomposing; but on heating the mixture, carbonic acid is immediately evolved, and ethylamine produced together with sulphovinic acid:

$$C^{10}H^{11}NO^4 + 2(HO,SO^3) = 2CO^2 + C^4H^7N + C^4H^6O^2,2SO^3.$$

(Wurtz, *N. Ann. Chim. Phys.* 42, 48).

Diethylurethane. $C^{14}H^{15}NO^4$? — Perhaps obtained by the action of cyanic acid upon ether:

$$C^6NH^5O^2 + 2C^4H^5O = C^{14}H^{15}NO^4.$$

The two liquids, however, exert very little action, if any, upon one another, even when enclosed together in sealed tubes, and subjected to very high temperatures and enormous pressures. On opening the tubes when cold, no evolution of gas was observed; and on distilling the contents, the original liquids were obtained unaltered; only at the end of the distillation, when the temperature had risen to 200°, there passed over a very small quantity of a liquid which might be diethylurethane; but the reactions obtained were not sufficiently marked to identify it (Wurtz).

END OF VOLUME IX.

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